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Gamma-ray analysis of atmospheric dust samples

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(Received 16 March 1959)

Abstract—The presence of nuclear weapon debris in the air over Canada following the tests in the spring of 1957 and 1958 was demonstrated by γ -ray spectral studies. Peaks from fission products Zr^{95} , Nb^{95} , Ru^{103} , Ce^{141} , Ce^{144} and Cs^{137} , with half-lives of several days and longer, were identified. The same peaks were found in a sample of house dust. Very long-lived fission products such as caesium-137 were not of sufficient activity to permit identification until the samples had decayed for several months.

INTRODUCTION

DURING several flights by the Geological Survey of Canada over Arctic islands there were indications of airborne radioactivity measurable with a portable scintillation counter. The areas of activity appeared to shift in conformity with the wind pattern. A dust sample collected in a filter mounted in the aircraft had readily detectable γ -ray activity. To verify the possibility that the airborne activity might be related to ore deposits, a series of dust samples was collected during flights out from Churchill, Manitoba, beginning in May 1957, and again in 1958 during flights in the Gulf of St. Lawrence region. Records pertaining to the flights were kept for use in the event that there proved to be significant differences in the samples. Additional dust samples were collected from the ground for purposes of comparison.

The γ -ray spectra of the samples were determined at the Mines Branch laboratories of the Department of Mines and Technical Surveys in Ottawa and compared with those of the natural radioactive emitters: potassium, thorium and uranium, including their daughter elements. With the exception of one sample none of the γ -activity could be attributed to natural emitters, but rather to atomic weapon debris. A series of nuclear explosions had taken place in Siberia terminating in mid-April 1957, a few weeks before the first sample was collected (TERENTIUK, 1958).

Many investigations of fall-out activity have been reported, mainly based upon a determination of total β -activity, or upon the measurement of such fission products as strontium-89, strontium-90 after radiochemical separation. In contrast very little information has been published concerning the various γ -ray emitters actually found in the atmosphere. The relative importance of these emitters has been found to vary with the time of sampling and is clearly related to the time elapsed since the last nuclear tests. A paper by HUNTER and BALLOU (1951) provides a graph which is useful for estimating the relative proportions of the most active fission products remaining at the end of various intervals after fission. Considering the dates when the spectra were first determined (24, 29 May 1957), and the known dates of the last previous atomic test explosions (up to mid-April, 1957, TERENTIUK, 1958) it is reasonable to assume that at least 40 days

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had elapsed since the last atomic test to the sampling dates. Since much of the activity in a sample was found to decay within a few months, the cumulative effect of tests of previous years was expected to be confined to a few very long-lived nuclides only. Attempts to measure the spectrum of several combined samples failed to show peaks due to caesium-137 (more strictly due to barium-137, the short-lived daughter of Cs^{137}), and other very long-lived fission products, until the activity of the samples had decayed for several months after collection. Such γ -ray determinations supplement recent β -ray measurements on atmospheric dust samples (TERENTIUK, 1958) and measurements of total activity by SOLON *et al.* (1958) and ARGIERO *et al.* (1958).

EXPERIMENTAL DETAILS

The spectrometer contained a 2 in. by 2 in. cylindrical sodium iodide crystal as the scintillation detector. The crystal was mounted against a RCA type no. 6655 photomultiplier tube in a magnesium container. A thin aluminium-foil window was cemented in that end of the container to which the sample was exposed. The scintillation counter output was fed to a pulse-height analyser. The dust was collected in a cloth filter 4 in. by 8 in., folded once to 4 in. by 4 in. size. This was wrapped in paper with one thickness separating the filter from the aluminium window in the detector enclosure.

The method of collection employed during the series of flights in 1957 was less efficient than the one adopted during the following year. At that time a scoop directed air from outside the aircraft against or through the filter. In 1958 the filter was mounted directly on the nose of the aircraft. No attempt was made to cover the filter at take-off and on landing, so that a significant proportion of the dust may have been collected at these times.

A few attempts were made at sample concentration to increase the activity in the search for weak long-lived emitters and to produce a more stable sample geometry for half-life determinations. Filters were washed with chloroform which was then evaporated; other filters were dissolved in hot nitric acid; the simplest and most convenient method was to compact a number of fine filters in a thin aluminium sample dish with a tightly-fitted cover, using a hydraulic press.

Each filter in the aircraft was exposed at a constant altitude of 1000 ft, during three or four flights of 6 hr duration at an airspeed of 180 miles/hr. The dust picked up at take-off and upon landing was not expected to differ in the proportions of the active emitters present; however, to determine whether there was measurable activity, a ground sample was secured from the contents of a household vacuum-cleaner bag in use during May and June 1958. The effects of the atom-bomb tests of March 1958 were quite evident, as the total γ -activity of the contents, measuring several rather bulky fractions, was in excess of 7000 counts/min for a 2 lb sample.

DISCUSSION OF RESULTS

Table 1 shows the contribution to the total activity of the most active γ -emitters from 40 to 320 days after fission, and also their principal γ -peaks. Other nuclides, such as strontium-89 and strontium-90, which are known to be produced in fission are not listed as they emit β -particles only. Figs. 1-7 illustrate spectra of samples

Table 1. Radiation from fission products

Nuclide	Half-life	Percentage of total activity (β and γ) (days after fission) [†]				Principal γ -ray levels* (SMITH and FARMELO, 1958) (keV)
		40	80	160	320	
Ce ¹⁴¹	33 days	12	9	4	—	142
Zr ⁹⁵	65 days	10	14	15	9	723, 756
↓						
Nb ⁹⁵	35 days 90 hr	7	16	25	18	765 236
Ba ¹⁴⁰	13 days	9	3			30, 132, 160, 304, 436, 537
↓						
La ¹⁴⁰	40 hr	10	3			328(40), 490(50), 815(46), 1600(100)*
Ru ¹⁰³	40 days	6	8	5	1	498(100), 610(7)
↓						
Rh ¹⁰³	57 min					I.T.
Nd ¹⁴⁷	11 days	3				92, 530
↓						
Pm ¹⁴⁷	2.6 years			1.5	5	121
Ce ¹⁴⁴	285 days	3	5	10	23	33.7(7), 81(17), 134(29)
↓						
Pr ¹⁴⁴	17 min					695(12), 1480(2.3), 2180(5.9)
I ¹³¹	8.1 days	2				80(6), 280(6), 364(81), 637(9), 722(2.8)
Xe ¹³³	5.3 days	1				81
Ru ¹⁰⁶	1.0 year				2	No γ , parent of Rh ¹⁰⁶
↓						
Rh ¹⁰⁶	30 sec					513(100), 624(53), 1045(8)
Cs ¹³⁷	27 years				1	No γ , parent of Ba ¹³⁷
↓						
Ba ¹³⁷	2.6 min					662

* Nos. in parentheses indicate relative intensity for each isotope.

[†] HUNTER and BALLOU (1951).

from different locations and at various stages of radioactive decay. The activity of the samples differed owing to factors such as exposure time, and meteorological conditions; however, all spectra at the same stage of decay were essentially the same despite the wide separation of the regions in this country where they were

collected. Since there is evidence that most of the fall-out activity continues to circulate in latitudes close to that in which the test explosion took place (ANON., 1958) it is improbable that shorter-lived nuclides will reappear in significant amounts from more recent tests in the southern hemisphere.

Calibration was carried out in two principal energy ranges, from 100 to 1000 keV and from 20 to 200 keV, the former using Na^{22} , Cs^{137} and Mn^{54} , and the latter

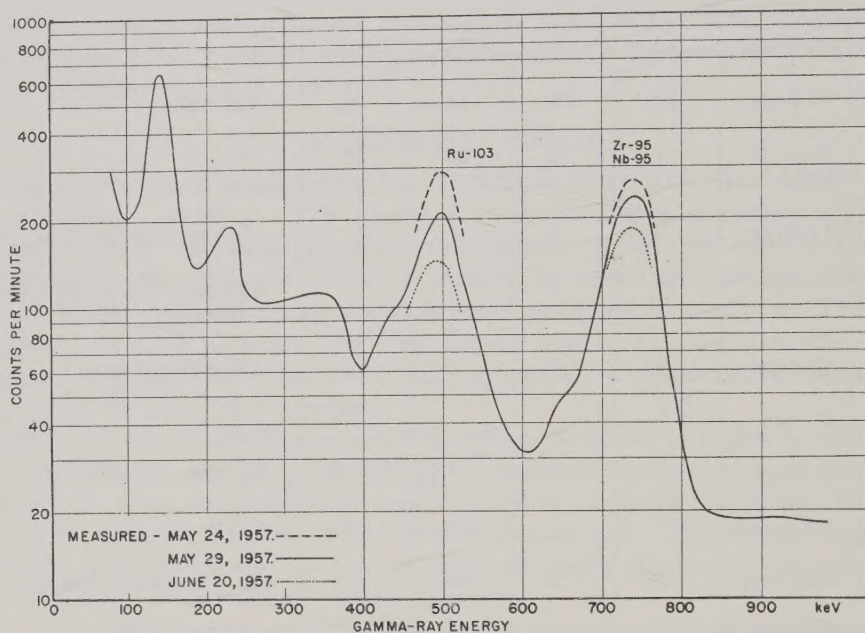


Fig. 1. Sample 1 (1957), three measurements shortly after collection.

Cs^{137} (32 keV X-ray line) and Co^{57} , for comparison peaks. The standard calibration samples were separated from the detector sufficiently to have a count rate of the same order as that from the dust sample, to minimize shift in gain with count rate (CALDWELL and TURNER, 1954). Because of the number of fission products present, each peak was usually composed of more than one unresolved γ -ray, a factor which added greatly to the problem of identification. A recent list of principal γ -ray energies has been prepared by SMITH and FARMELO (1958).

Fig. 1 presents the complete γ -ray spectrum of a typical dust sample above 100 keV, with a comparison of peak counts at three successive dates. Two main peaks of energies 500 and 740 keV are clearly evident. The widths of the two peaks are greater than would be obtained from a monoenergetic γ -ray in the same energy region; namely; the 662 keV line from Cs^{137} , for which 8 per cent resolution was obtained. The rate of decay of the 500 keV peak appeared to be more rapid initially. This might be attributed to 13 day Ba^{140} emitting at 436 and 537 keV; additional evidence is obtained in Fig. 7, where there is shown an early decay in the 160 keV region of the 1958 samples. Most of the activity is, however, due to 40 day Ru^{103} at 498 keV; this peak was evident for about 1 year.

The other major peak is 65 day Zr^{95} (723, 756 keV) in combination with its daughter element, 35 day Nb^{95} (765 keV). The low energy region is indicated more fully in Fig. 2 which shows the complete spectrum over the range from 20 keV to 900 keV for a 1957 sample taken 6 months after collection. In Figs. 1 and 2 the 662 keV peak of Cs^{137} possibly shows as the slight hump on the lower edge of the 740 keV peak; it does not show up distinctly, however, until the sample is more

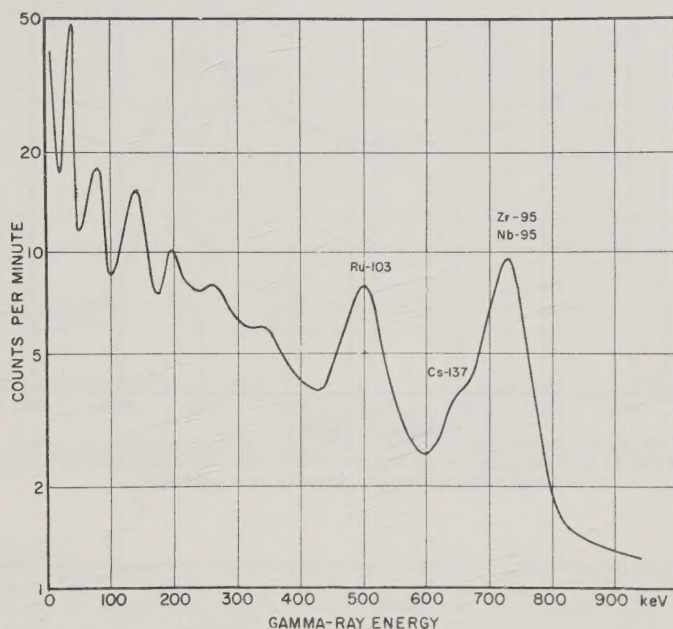


Fig. 2. Samples 12 and 15 (1957) measured 17 December, 1957 (count rate normalized to about that of a single sample for purposes of comparison).

than 1 year old; see Fig. 3, measured 12 August, 1958, in which the 662 keV γ -ray has emerged as the dominant activity.

A dust sample taken in the laboratory and a sample of house dust collected in a canister vacuum cleaner in Ottawa exhibited spectra of the same general shape as that shown in Fig. 2.

The spectra shown in Fig. 4 are those of the first 1958 sample, which was obtained over Eastern Ontario. The next group of samples in 1958 was obtained over the Gulf of St. Lawrence. These all show the same spectral shape. The spectrum in Fig. 5, extended to 2750 keV, shows by the absence of peaks at 1800 and 2600 keV that measurable quantities of thorium and uranium dust (in secular equilibrium) were not present. As there is no evidence of the 1600 keV peak of La^{140} , the daughter of Ba^{140} , in these spectra, the fall-out atoms in the samples were probably from 2 to 3 months old.

The spectrum shown in Fig. 6 was obtained on 29 October 1958, from a sample collected 13, 17, 21 and 22 October between Ottawa and the Gulf of St. Lawrence. It clearly indicates fission products which were only a few weeks old. The 1600 keV peak of lanthanum-140, daughter of 13 day barium-140, is quite evident in regard

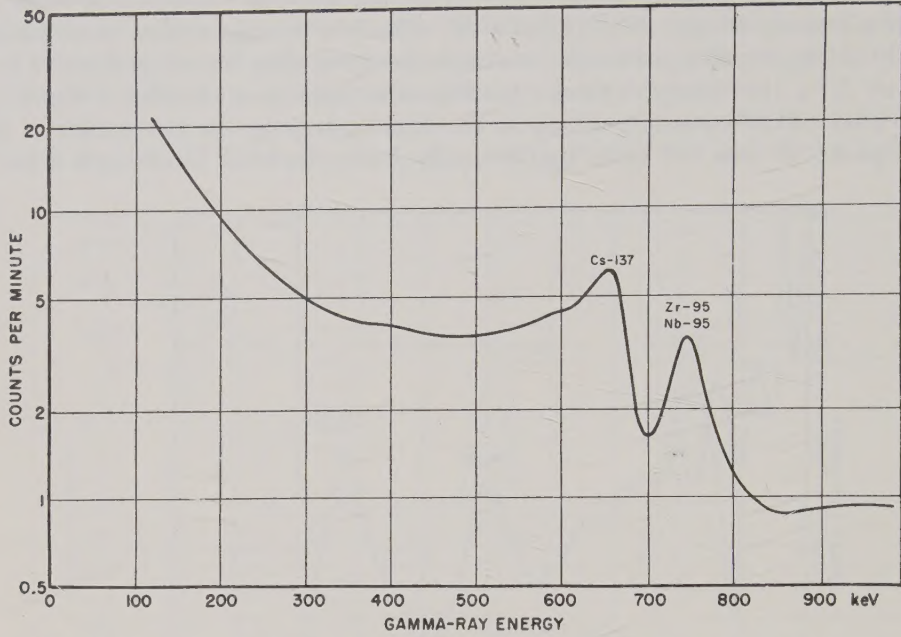


Fig. 3. Samples 4 to 15 (1957) measured 12 August, 1958 (count rate normalized to about that of a single sample for purposes of comparison).

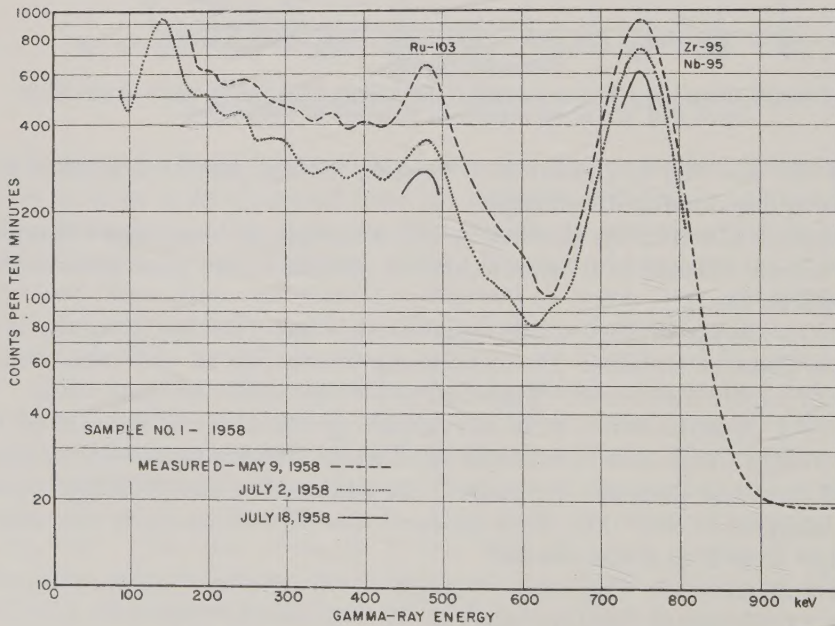


Fig. 4. Sample 1 (1958), the first three determinations.

Gamma-ray analysis of atmospheric dust samples

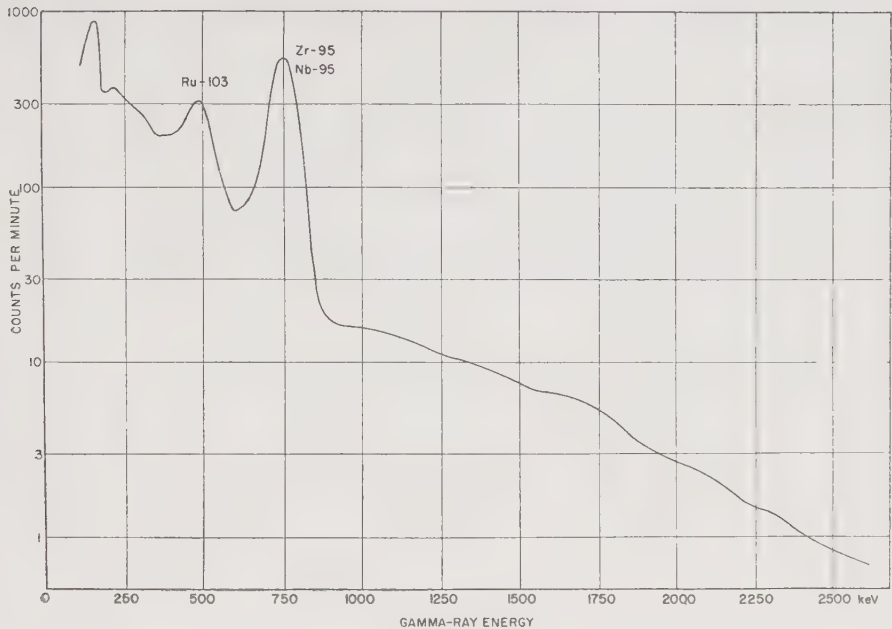


Fig. 5. Samples 1, 2 and 3 (1958), extended spectrum, 16 June, 1958.

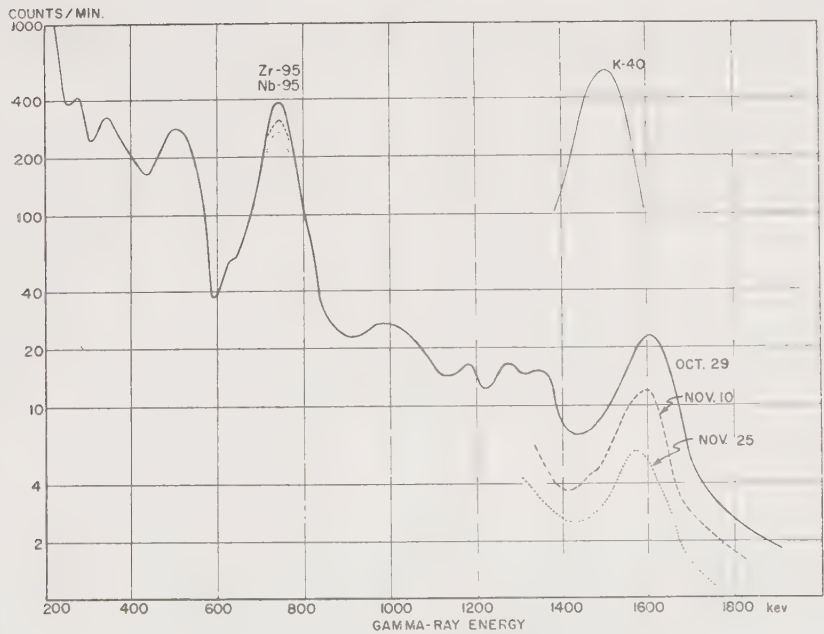


Fig. 6. Spectrum of dust sample showing La^{140} peak.

to energy: the nearest calibration peak was potassium-40 at 1460 keV; and in regard to half-life, the relative change in height of this peak in comparison with the other main peaks was noticeable after 2 days. The principal peaks are compared

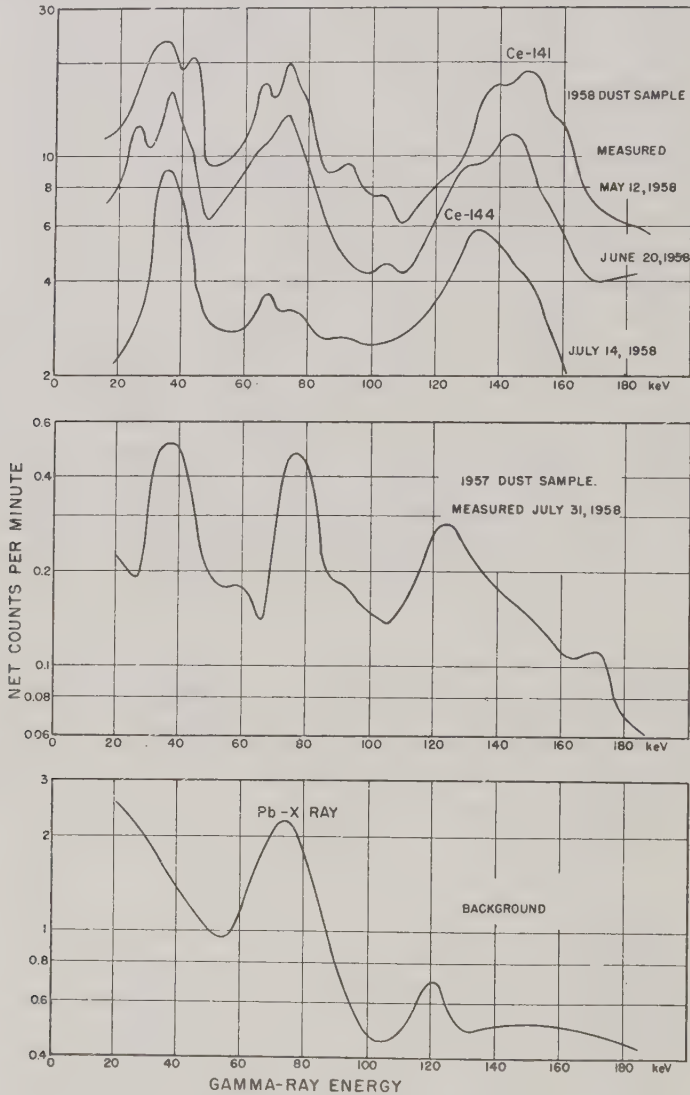


Fig. 7. Low-energy spectra.

after a 12 day, and a 27 day interval on the figure; the height of the 1600 keV peak above the continuum decreased with a half-life value of 13 days.

Spectra obtained in the low-energy region are shown in Fig. 7. The early decay in the 1958 sample around 160 keV has already been noted. In the same general peak the decay rate at 142 keV matches that of 33 day Ce^{141} , and the residual peak in the 1957 sample at about the same energy is identified as 285 day

Ce^{144} at 134 keV. These peaks cannot be resolved without radiochemical separation; it is therefore necessary to observe the gradual shift in energy of the combined peak and to rely on half-life estimates.

A peak due to X-rays from lead at 72.6 keV is clearly shown in all the low energy curves in Fig. 7 except that of 14 July 1958, when a small block of lead used to press the sample down against the crystal enclosure was omitted. In this case a thin lead sheet ($\frac{1}{16}$ in.) placed over the sample caused the peak to reappear at close to its previous intensity. The spectrum of the background clearly shows the peak where higher energy background radiation is producing X-rays in the walls of the lead castle.

To investigate the presence of short-lived emitters in the atmosphere, dust samples have been taken on the roof of the laboratory in Ottawa. Radon decay products as well as nuclear weapon debris were identified in these spectra. The sample collection time was reduced from 60 to 20 min with the result that the spectral peaks due to the radon daughters became relatively much more prominent. Most of this initial γ -activity was due to bismuth-214, identified by the rapid decay of its four peaks at 609, 1120, 1400 and 1760 keV. Thus the presence of free radon in the atmosphere is clearly indicated.

CONCLUSIONS

These measurements show that there is little change in the relative proportions of products from nuclear tests in air samples collected over wide areas of the country. The principal variation occurs as a result of the time elapsed since the last series of nuclear tests in the same hemisphere, and also the time between sample collection and measurement which will determine whether radon products will be the principal sources of γ -radiation to be detected. Identification of general background radiation will require *in situ* measurement with energy discrimination.

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Helium, neon and argon isotopes in some iron meteorites*

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Abstract—The cosmic ray produced He^3 , He^4 , Ne^{20} , Ne^{21} , Ne^{22} , Ar^{36} and Ar^{38} have been measured in seven iron meteorites with varying helium contents. The results on isotope abundance agree well with previous results. By considering the He^3/He^4 , $\text{He}^3/\text{Ne}^{21}$ and $\text{He}^3/\text{Ar}^{38}$ ratios it is shown that it may be possible to determine the depth at which a sample was in the original meteoroid from these ratios, rather than from the absolute amount of any particular isotope.

I. INTRODUCTION

It has recently been shown by PANETH *et al.* (1953) that cosmic rays produce measurable amounts of helium in meteorites during their flight through space. This result has stimulated studies to measure other cosmic ray produced isotopes. By measuring the amounts of stable and radioactive nuclides it seems feasible to obtain information on the composition and history of cosmic rays in space as well as shed some light on the question of the origin of meteorites.

Cosmic ray produced argon has been found by GENTNER and ZÄHRINGER (1957) and cosmic ray produced neon has been found by REASBECK and MAYNE (1955). Thus, all the rare gases below iron are produced by cosmic rays in iron meteorites.

FIREMAN and SCHWARZER (1957) measured He^3 by neutron activation and T by direct counting in two iron meteorites with known dates of fall. From the He^3/T ratio it is possible to calculate a cosmic ray exposure age. The result for the two meteorites was about a billion years. BEGEMANN *et al.* (1957) made a similar measurement for the stone fall of 1947, Norton County, and reported a cosmic ray exposure age of 260 million years.

Recently such exposure ages have been calculated from the amount of a spallation isotope alone, usually the helium, e.g. MARTIN (1953), EBERT and WÄNKE (1957), WÄNKE and HINTERBENGER (1958) and EHMANN and KOHMAN (1958). Calculations using the stable elements alone are based on fragmentary production cross-section results. In addition, the depth of the sample in the original meteoroid in space is not known. Then there are uncertainties concerning the primary cosmic ray flux in space both as to intensity and energy distribution. Finally, it is likely that a sizeable fraction of the nuclear interactions are produced by a complex array of secondary particles produced in the iron by the primary cosmic ray protons. For these reasons, at present, ages calculated on the basis of a stable isotope alone are at best very uncertain. It seems to us that a careful study of the helium, neon and argon contents of some iron meteorites, together

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with a set of reliable exposure ages determined by measuring the cosmic ray flux with a long-lived nuclide might lead to a basis for calculating exposure ages from the rare gas contents alone.

The purpose of the present experiments is to extend the measurements of helium, neon and argon in iron meteorites by determining all the isotopes in the same sample. In this way, one can obtain information concerning the variations in the various isotopic ratios. It has been pointed out (GENTNER and ZÄHRINGER, 1957) that the He : Ne : Ar ratios will depend on the depth in the meteorite.

The best set of samples would be a set taken from different depths in a very large meteorite. Such a set was not available to us, so we selected a group of meteorites with a widely varying helium content in the hope of obtaining some relations between the helium content and the amounts of the various isotopes.

Assuming a homogeneous cosmic radiation in space, the difference in the ratios may be due either to the amount of shielding during the passage of the meteoroid through space or to the time of exposure to cosmic rays. If the meteoroids all had a regular shape and the same exposure times then the amount of helium or any rare gas would represent a depth scale, that is, it would represent how far the specimen measured was below the surface of the original meteoroid. Also under these conditions, for the same amount of He⁴, viz. the same depth, a given ratio as He³/He⁴ or Ne/Ar, etc., would always be the same. So then, if these ratios are not constant it will be evidence for varying exposure ages.

II. EXPERIMENTAL

For the extraction and cleaning of the gas, a line was constructed of special glass (Corning combustion tubing 1710), which has a low helium leakage. Only mercury cut-offs or metal valves were used. The sample was melted rapidly by induction heating in a graphite crucible. The crucible was surrounded by a quartz tube to protect the combustion tubing from evaporated material. The wall of the furnace was cooled with water. The extracted gases were reacted over Zr or Ca and CuO. As furnaces, Kovar tubes with quartz liners containing these chemicals, were directly sealed to the line. A high sensitivity mass spectrometer was connected to the sample line (SCHAEFFER, 1960). The spectrometer tube was made of Pyrex glass and coated with SnO₂ on the inside. A specially constructed ion source with sapphire insulators provided a low background. For the ion detection a Dumont SP 102 multiplier was used. The spectrometer was baked at 350°C, then closed by metal valves from the pump and sample line. Further evacuating was achieved by pumping with the ion gauge. For a measurement, the valve to the sample line was opened and the whole spectrometer was filled with the sample gases. The valve was closed again and the isotopic analysis could be made. The peaks were stable for several hours.

For calibration a standard mixture of He³, He⁴, Ne and Ar was prepared. The pressures were measured by a McLeod manometer. Small amounts, comparable to the sample, could be added to the mass spectrometer by volume dilution. Thus the increase of the peak height can be compared with the unknown quantity of the sample gas under the same conditions. After each determination the sample was remelted at a slightly higher temperature. The second meltings usually

yielded below 5 per cent of the amounts of rare gases found in the first melting. When such a blank run happened to be above 10 per cent the data were discarded.

III. DESCRIPTION OF THE METEORITES

Arispe is a coarsest octahedrite which was found in 1896 in Mexico. Several large masses, 272, 116, and 20 lbs, contains 6.77% Ni. The piece used in this research was obtained from Wards Natural Science Establishment.

Canon Diablo is a medium octahedrite found in Arizona in 1891. Numerous fragments from minute pieces to pieces over 1000 lb: total mass found over 30 tons; contains 7.17% Ni. The sample used in this research was obtained from the American Museum of Natural History, N.Y. specimen no. 827 through the courtesy of B. MASON.

Casas Grandes is a medium octahedrite found in Mexico in 1867. One piece 3407 lb; contains 7.74% Ni. For this research chips were obtained from the Smithsonian Museum, Washington, D.C. through the courtesy of E. P. HENDERSON.

Odessa is a coarse octahedrite found in Texas before 1922. Many small pieces found, over 600 lb in all; contains 8.73% Ni. The sample used in this research was specimen no. 33.20 obtained from Wards Natural Science Establishment, Rochester, N.Y.

Sikhote-Alin is a coarsest octahedrite or a granular hexahedrite which fell in Eastern Siberia 12 February, 1947. Many fragments found, several tons in all, contains 5.8% Ni. The sample used in this research was from the piece The Far East, specimen no. 2052. obtained through the courtesy of E. KRINOV from the Academy of Sciences, U.S.S.R.

Toluca is a medium octahedrite known before 1776 from Mexico. Many masses have been found, contains 8.3% Ni. The sample used in this research was catalogue no. 729 of the American Museum of Natural History obtained through the courtesy of B. MASON.

Williamstown is a medium octahedrite found in Kentucky in 1892. Only one mass of 68 lb was found; contains 7.26% Ni. The sample used in this research was specimen no. 800 of the American Museum of Natural History obtained through the courtesy of B. MASON.

IV. RESULTS

Table 1 shows the quantities of noble gases obtained by the mass spectrometric analysis. The numbers are mean values of at least two measurements. In cases

Table 1. Experimental results of He-, Ne- and Ar-measurements in seven iron meteorites in units of 10^{-8} cm³

Meteorite	He ⁴	He ³	He ³ /He ⁴	Ne ²¹	Ne ²⁰ : Ne ²¹ : Ne ²²	Ar ³⁶	Ar ³⁸	Ar ⁴⁰	Ar ³⁶ cor. *	Ar ³⁸ cor./Ar ³⁶ cor.
Williamstown	1920	480	0.25	6.0	1 : 0.8 : 0.9	17.6	26.4	52	17.4	1.5
Arispe	930	270	0.29	2.3	1 : 1 : 1	5.5	8.9	13.7	5.5	1.6
Odessa	710	220	0.31	2.3	1 : 0.9 : 1	7.0	12.0	10.1	7.0	1.6
Sikhote-Alin	481	130	0.27	1.5	—	2.8	4.1	16	2.8	1.5
Casas Grandes	370	130	0.35	1.0	—	2.4	3.6	18	2.4	1.5
Toluca	295	100	0.34	0.8	—	1.7	2.4	15	1.7	1.5
Canon Diablo	42	4.2	0.10	0.11	—	0.27	0.44	16.7	0.27	1.7

* The correction is for the air argon contamination.

where the discrepancy was more than 5 per cent three or more samples have been investigated. No correction for the background of the spectrometer was necessary. Except as indicated below such corrections are less than a few per cent.

The values for Ne^{20} and Ne^{22} of meteorites with low amounts of helium have high backgrounds and the results have been discarded. The Ar^{40} content is mainly due to air contamination as shown by blank runs. In some cases a contribution of radiogenic Ar^{40} due to the K-decay cannot be excluded. This will not affect the $\text{Ar}^{36} : \text{Ar}^{38}$ ratio appreciably, however. In Fig. 1 the relations between

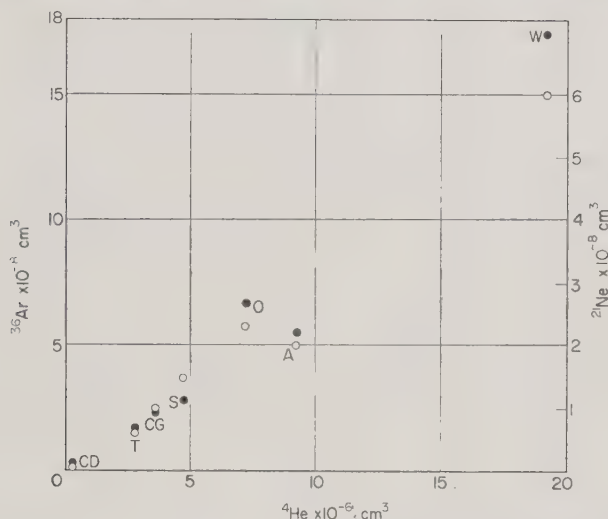


Fig. 1. Argon-36 and Neon-21 relative to Helium-4 in several iron meteorites. CD, Canyon Diablo; T, Toluca; CG, Casas Grandes; S, Sikhote-Alin; O, Odessa; A, Arispe; W, Williamstown ● Argon-36; ○ Neon-21.

He^4 , Ar^{36} and Ne^{21} is presented. The amount of Ar^{36} and of Ne^{21} increases with the He^4 content. The air contamination argon was always so small that the contribution to the Ar^{36} and Ar^{38} contents of the meteorite was negligible.

The calculated $\text{He}^4/\text{Ne}^{21}/\text{Ar}^{36}$ ratios are given in Table 2. All these results are in general agreement with the data of other authors. EBERT and WÄNKE (1957)

Table 2. He^3/He^4 , $\text{He}^3/\text{Ne}^{21}$ and $\text{He}^3/\text{Ar}^{36}$ ratios

Meteorite	He^3/He^4	$\text{He}^3/\text{Ne}^{21}$	$\text{He}^3/\text{Ar}^{36}$
Casas Grandes	0.35	130	54
Toluca	0.34	125	58
Odessa	0.31	95	33
Arispe	0.29	117	49
Sikhote-Alin	0.27	87	46
Williamstown	0.25	80	28
Canon Diablo	0.10	38	16

and VINOGRADOV *et al.* (1957) found values from 100 to 134 for the $\text{He}^3/\text{Ne}^{21}$ ratio. WÄNKE and HINTENBERGER (1958) found the He/Ne ratio in several iron meteorites to vary between 131 and 188. The $\text{Ne}^{20}/\text{Ne}^{21}/\text{Ne}^{22}$ ratio of 1 : 0.9 : 1 is in agreement with the ratio of WÄNKE and HINTENBERGER (1958) and differs from REASBECK and MAYNE (1955) value of 1 : 0.84 : 0.49. The $\text{Ar}^{38}/\text{Ar}^{36}$ ratio is the same as that reported by GENTNER and ZÄHRINGER (1957). Also the $\text{He}^3/\text{Ar}^{38}$ ratios are within the values obtained in their research. The recent publication of GERLING and LEVSKII (1958) on Sikhote-Alin is also in good agreement.

V. DISCUSSION

From Table 1 can be seen that high He^3/He^4 ratios are not correlated with high amounts of He^4 or He^3 . If all the meteorites would have been exposed to the same flux of cosmic radiation the amount of spallation isotopes and also the He^3/He^4 ratio should be characteristic for the kind of irradiation and hence for the depth the sample was taken from. By penetrating material the cosmic ray particles lose energy and samples from the inside of a meteorite (preatmospheric size) have been bombarded by relatively lower energy particles. To aid in the interpretation of the meteorite data, irradiations of iron targets have been performed at different proton energies, and He, Ne and Ar cross-sections were measured (SCHAEFFER and ZÄHRINGER, 1959). These investigations gave He^3/He^4 ratios increasing with energy and always higher cross-sections for the He^3 production than for T production. Therefore one would expect a He^3/He^4 ratio decreasing with depth in the meteorite. This is what has been observed in the meteorites Grant (HOFFMANN and NIER, 1958; FIREMAN, 1959) and Carbon (FIREMAN, 1958).

If the primary cosmic radiation contains appreciable low energy particles, which is indicated by recent experiments (NEHER, 1958; GENTNER *et al.*, 1958) the surface may have additional spallation products. The He^3/He^4 ratio (not the He^3 content) may therefore be lower at the surface. In this way the high helium content and the low He^3/He^4 ratio of the Williamstown meteorite could be understood. Alternatively Williamstown may have a long exposure age. The low helium content and the high helium ratio of the Casas Grandes and Toluca samples, however, are not understandable by depth variation alone. One is tempted to assume that these samples had different times of irradiation out in space. They must have been irradiated by high energy particles for a shorter time of exposure. There is evidence that exposure ages of meteorites do vary as shown by the results of FIREMAN and SCHWARZER (1957) and BEGEMANN *et al.* (1957).

Arranging the results according to the He^3/He^4 ratios and calculating the $\text{He}^3/\text{Ne}^{21}$ and $\text{He}^3/\text{Ar}^{36}$ ratios as done in Table 2 allows a better understanding of the results. The $\text{He}^3/\text{Ne}^{21}$ and the $\text{He}^3/\text{Ar}^{36}$ ratios decrease with the helium ratios from 130 to 38 and 58 to 16 respectively. There is only one exception, the Odessa sample which has high neon and argon values. (This sample has perhaps been heated to a higher temperature and diffusion losses have caused a decrease of the He.)

In the case of the He^4 it is possible that some of the He^4 is produced from the decay of uranium in the meteorite. Recently a meteorite has been found (SCHAEFFER and FISHER, 1959), Washington County, which has a very high He^4/He^3

ratio; about five times that of meteorites with comparable He^3 and other rare gas isotopes. So it may be that some of the He^4 in the iron meteorites measured in this paper is also from helium decay.

The rapid change of these ratios with the He^3/He^4 values can be understood since the target measurements also show a much higher He^3 production at higher bombarding energies, while the neon and argon cross-sections are not very dependent on the energy above about 1 BeV (FRIEDLANDER, private communication; FIREMAN and ZÄHRINGER, 1957; SCHAEFFER and ZÄHRINGER, 1959). Thus the He^3/He^4 , $\text{He}^3/\text{Ne}^{21}$ or $\text{He}^3/\text{Ar}^{38}$ ratio rather than the absolute amount of spallation isotopes can represent a depth scale. Perhaps these few cases are not enough to show conclusive evidence. Further experiments therefore are in preparation.

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The abundance of the rare earth elements in relation to their origin

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Abstract—The abundances of the rare earth elements given by SUESS and UREY (1956) are correlated with the processes of formation of the individual nuclides listed by BURBIDGE *et al.* (1957). It is shown that the smoothing process carried out by SUESS and UREY leads to relative depression of the *s*-process nuclides and elevation of those formed by the *r*-process. Later abundances published by CAMERON (1959b) accentuate this trend. His Ce/Nd ratio necessitates major fractionation between the earth and chondrites.

INTRODUCTION

THE rare earths constitute the only large group of chemical elements not liable to serious fractionation in the earth.* It has been thought that their relative abundances may therefore still reflect an "initial" abundance pattern, and so provide critical evidence for theories of nucleogenesis. The close geochemical coherence of this group has frequently been stressed. "We can therefore expect in the group of rare earth elements the closest approximation to 'primordial' or even 'original', relationships between mass number, nuclear charge and abundance of atomic species" (GOLDSCHMIDT, 1954, p. 313). "The rare earths have very similar chemical properties so that separation of these elements approached in difficulty the separation of isotopes and in these rare earth elements we find a marked regularity of abundances. . . . It was recognized . . . that this meant that the abundances of isotopes should similarly represent a definite regularity, and that elementary abundances should be such that all nuclides should vary in some regular way" (SUESS and UREY, 1956, p. 54).

Significant advances in our understanding of the formation of the elements have been made recently, principally through the work of BURBIDGE *et al.* (1957) and CAMERON (1959a). Their results in conjunction with the evidence from astrophysical studies on stellar populations (O'CONNELL, 1958) have reorientated thought on the whole question of elemental abundances. It is now apparent that abundance data from the sun, meteorites and earth may provide us with the composition only of the original dust and gas from which these units condensed. As BURBIDGE *et al.* (1957) have pointed out, this is to some degree, an accidental composition, very dependent on time and place of formation in our galaxy. The estimation of "galactic", "primitive", "universal", "primordial", "original" or

* In a reducing environment, the formation of Eu^{2+} leads to the separation of this element (GOLDSCHMIDT, 1954, p. 316). Ce^{4+} might be formed in a strongly oxidizing environment but the high value of the fourth ionization potential of cerium (36.5V) and the magnitude of the difference (17V) from the third ionization potential make this event unlikely. Fe^{2+} is more readily oxidized to Fe^{3+} than is Ce^{3+} to Ce^{4+} and hence Ce in chondrites should be trivalent since most of the iron is divalent. In a sedimentary environment, where the oxidation states will be similar to those in aqueous solution, Eu will be trivalent. No selective effects based on oxidation to Ce^{4+} seem evident.

“cosmic” abundances is a problem of a different order of magnitude. The composition of the solar system is dependent in detail on the extent to which the products of the various element forming processes became incorporated in the dust and gas.

Eight processes of nucleogenesis are listed by BURBIDGE *et al.* (1957). Three of these, the *s*-, *r*- and *p*-processes, together with contributions from fission, have been suggested to be responsible for the formation of the rare earth nuclides. The *s*-process refers to neutron capture on a long time scale (intervals between successive neutron captures of ~ 100 to $\sim 10^5$ years) which is thought to take place in red giants and super-giants. Clear evidence of the operation of the *s*-process has been provided by BURBIDGE and BURBIDGE (1957) from observations on the giant Ba II star, HD 46407. Compared with a normal star, La, Ce, Pr, Nd, Sm, Gd and Yb of the rare earths are over-abundant by factors of 10 or more. The steady emission of matter from red giants and super-giants and the enrichment of the interstellar material in the products of the *s*-process has been discussed by DEUTSCH (1956) and BURBIDGE *et al.* (1957, Section XII A and Table XII.1). The *r*-process involves neutron capture on a short time scale (0.01 to 10 sec) and takes place, with the *p*-process, of minor importance, in supernovae. From consideration of the rate of dispersal of material from supernovae, the time for the solar system to condense from interstellar material ($10^7 - 10^8$ years), and the frequency of supernovae, BURBIDGE *et al.* (1957, p.639) think that it is not impossible that all the *r*-process isotopes in the solar system may have been produced in one supernova.

The amounts of the *s*- and *r*-process nuclides are therefore dependent on different nuclear processes, taking place at differing rates, and in different environments. There is consequently, no simple fundamental relationship between the relative abundances in the solar system of nuclides produced by the *s*- and *r*-processes. The nuclides resulting from the *r*-process might well be very much more or less abundant depending on the frequency of supernovae. Since that closely similar group of elements, the rare earths, are formed by several processes, it is of interest to examine their relative abundances and apparent regularities, particularly for the odd-*A* nuclides, and to see whether they reflect the different origins indicated by the astrophysical results. It is first necessary to investigate the raw material for these calculations, the analytical data for the rare earth elements in the earth and meteorites.

DATA ON ELEMENT ABUNDANCES

GOLDSCHMIDT (1937) published a classic diagram comparing abundances of the group in the sun (RUSSELL, 1929), shales (MINAMI, 1935), chondrites (NODDACK, 1935) and rare earth minerals (GOLDSCHMIDT and THOMASSEN, 1924). NODDACK (1935) using an X-ray spectrographic method of analysis provided data for the whole group in chondrites.* For common crustal material, only the determinations on sediments by MINAMI (1935) using a similar technique are complete for all rare earth elements. Both these sets of data are given in Table 1. NODDACK found a

* LEVIN *et al.* (1957) give a table of the average chemical composition of all meteorites. This reference is a summary of a paper in *Meteoritika* **14**, 38-53, (1956), which is not accessible. No separate data for chondrites are given. La is very abundant (200 p.p.m.) compared with Ce (2 p.p.m.) and the other rare earth elements (0.3-1.7 p.p.m.).

distinctly different abundance pattern from that of MINAMI, the main points of difference being that in NODDACK's data, cerium is less abundant than neodymium, there is a peak at dysprosium, with a rather symmetrical distribution of the neighbouring elements, and the ratio of La and Ce to the heavy rare earths is low. The pattern found by MINAMI with its rather regular decrease of both odd and even numbered elements is very well known.

Table 1. Abundance data for the rare earth elements

Z	Element	* p.p.m. by wt.	* Nos. of atoms	* Nos. of atoms	† Nos. of atoms	‡ Nos. of atoms	§ Nos. of atoms	** Nos. of atoms
57	La	18.4	2.00	1.00	1.00	1.00	1.00	1.00
58	Ce	48.3	5.19	2.59	1.13	1.12	1.15	1.87
59	Pr	5.61	0.599	0.299	0.20	0.475	0.46	0.19
60	Nd	23.8	2.48	1.24	0.72	1.64	1.748	0.721
62	Sm	6.47	0.647	0.323	0.332	0.601	0.476	0.13
63	Eu	1.06	0.105	0.0524	0.093	0.158	0.230	
64	Gd	6.36	0.608	0.304	0.34	0.899	1.03	0.072
65	Tb	0.91	0.0862	0.043	0.048	0.285	0.18	0.0017
66	Dy	4.47	0.414	0.207	0.28	1.14	1.33	0.018
67	Ho	1.21	0.110	0.0552	0.059	0.323	0.36	0.0025
68	Er	2.47	0.223	0.111	0.16	0.937	1.166	0.0065
69	Tm	0.20	0.0177	0.0089	0.0159	0.165	0.18	
70	Yb	2.66	0.232	0.116	0.11	0.899	0.786	0.0021
71	Lu	0.66	0.0567	0.0283	0.025	0.291	0.0716	0.00033

* MINAMI (1935), SHALES.

† SUESS and UREY (1956), based on MINAMI.

‡ NODDACK (1935), CHONDRITES.

§ CAMERON (1959b), based on NODDACK.

** GAVRILOVA and TURANSKAYA (1958), GRANITE.

Other determinations of individual elements (La and Nd usually) have been made by many workers using emission spectrochemical analysis. Unfortunately Ce has a poor spectral sensitivity, and thus information on the La-Ce-Nd relation is not common. For the critical La-Ce-Nd ratios, it is mandatory to compare the results obtained by one analyst. BERMAN (1957) has provided data for these elements in G-1 and W-1 using a combined chemical enrichment-spectrochemical procedure. These samples represent rock types which are common in the crust. CHODOS (see AHRENS and FLEISCHER, 1960) has also provided similar data. EDGE (personal communication) has determined La/Ce and Ce/Nd ratios in thirteen granites and in G-1 and W-1 by a combined ion-exchange-optical spectrographic technique. The La/Ce ratios average 0.16 and the Ce/Nd ratios average 6.25. These samples have the same K/Rb ratio as chondrites (HERZOG and PINSON, 1956) and in addition W-1 has the same K/Cs ratio as chondrites (AHRENS, EDGE and TAYLOR, 1960), so no extreme fractionation process has selectively altered these critical ratios. GAVRILOVA and TURANSKAYA (1958) give abundance data on

twelve rare earth elements in the Kirovograd granite. Their results are given in Table 1 and these figures show a distribution pattern similar to that of MINAMI (1935).

The abundances from these sources are shown in Fig. 1(c) and indicate that Ce is more abundant by a large factor than Nd in these common rocks. By analogy

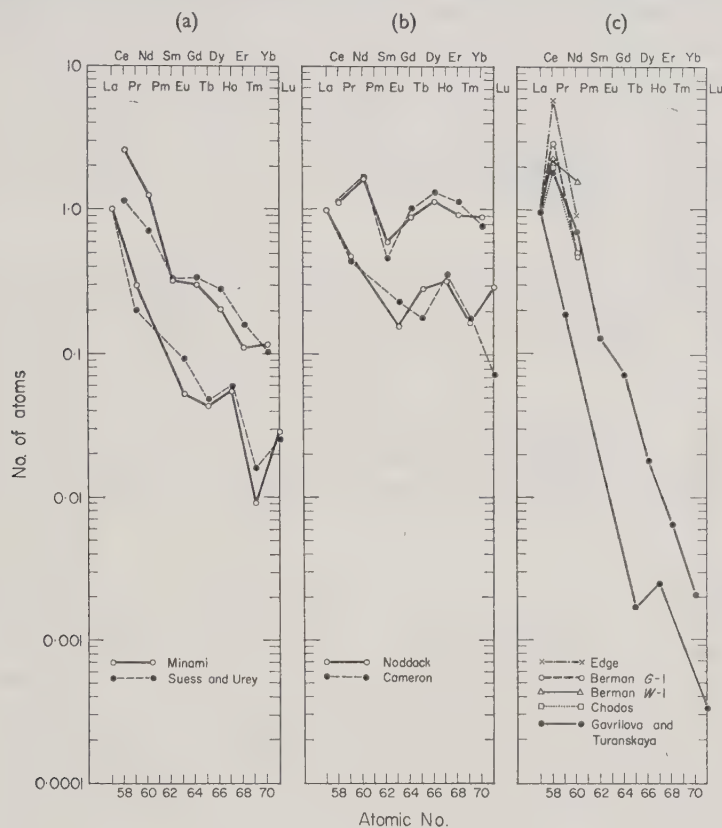


Fig. 1. Abundances of the rare earth elements plotted on a logarithmic scale against atomic number (Z). Data from the following sources: (a) MINAMI (1935) and SUESS and UREY (1956). (b) NODDACK (1935) and CAMERON (1959b). (c) BERMAN (1957), CHODOS (Ahrens and Fleischer, 1960), EDGE (personal communication), and GAVRILOVA and TURANSKAYA (1958).

All data are plotted relative to $\text{La} = 1.00$ atom.

with the K/Rb ratio and the known geochemical behaviour of K, Rb and the rare earths, it seems unlikely that the chondrites possess a Ce/Nd ratio of less than 1.

More data on the distribution of the group in rare earth minerals are given by BJØRLYKKE (1935), SAHAMA and VÄHÄTALO (1939), MURATA *et al.* (1953), BUTLER (1957, 1958), SEMENOV and BARINSKII (1958) and other workers. Their results have shown that anomalous rare earth assemblages occur in rare earth minerals from pegmatites. This sort of fractionation is analogous to the lowering of the K/Rb ratio by Rb enrichment in similar geological environments (TAYLOR *et al.*, 1956; HEIER and TAYLOR, 1959). There is, however, no change in the K/Rb

ratio in chondrites and terrestrial material in general.* SEMENOV and BARINSKII (1958) give data on the abundance of the rare earth elements in 138 minerals, mainly from pegmatites. It is interesting to observe that 107 of these minerals have a Ce/Nd ratio of greater than 1.0; four minerals (three euxenites and a gadolinite) have Ce equal to Nd (the data are given as wt.%) and twenty-seven minerals have Ce less abundant than Nd. These comprise one monazite, five samarskites, one euxenite, two fergusonites, one siderite, one aeschynite, two pyrochlores, eleven gadolinites, one chindusuite, one halloysite, two sphenes and one uraninite. If these samples represent any sort of adequate sampling, then only about one quarter of the rare earth minerals from pegmatitic or similar uncommon geological environments have a Ce/Nd ratio of less than 1.0, and the majority have Ce/Nd ratios similar to the common rock types. An instructive diagram is given by MASUDA (1957, Fig. 1).

In Fig. 1 are shown the abundances, in numbers of atoms relative to La = 1.00 from: (a) MINAMI (1935), SUESS and UREY (1956) (based on MINAMI); (b) NODDACK (1935), CAMERON (1959b) (based on NODDACK); (c) BERMAN (1957), CHODOS (AHRENS and FLEISCHER 1960), EDGE (personal communication), GAVRILOVA and TURANSKAYA (1958). It can be seen from the data of BERMAN, CHODOS, EDGE and GAVRILOVA and TURANSKAYA on granites that the Ce/Nd ratio is greater than 1 (see BUTLER (1957) for a discussion on this point). Thus the data for igneous rocks agree with that of MINAMI for sediments. Therefore, if NODDACK's data be accepted, we are faced with the necessity of major fractionation between the chondrites and the earth.

Most workers have felt that severe fractionation for such a closely coherent group was unlikely between the chondrites and sediments, and that the differences between NODDACK's data and MINAMI's data were due to analytical error. Considerations of this type led SUESS and UREY (1956) to use relative abundances from MINAMI, and to reject NODDACK's data. In particular, they used the more or less regular decrease of abundance of the odd-*A* nuclides as a true regularity, and adjusted MINAMI's data to fit a smooth curve. This does not seem to be a valid assumption (see next section).

ORIGIN OF RARE EARTH NUCLIDES

BURBIDGE *et al.* (1957) provide an extensive list of processes of element synthesis in stars, and discuss the formation of the rare earth nuclides in terms of the abundances of SUESS and UREY.

As can be seen from Fig. 1 the effect of the smoothing of MINAMI's data by SUESS and UREY (1956) has been to decrease the abundances of $_{58}\text{Ce}$, $_{59}\text{Pr}$, $_{60}\text{Nd}$; to increase the abundances of $_{62}\text{Sm}$, $_{63}\text{Eu}$, $_{64}\text{Gd}$, $_{65}\text{Tb}$, $_{68}\text{Dy}$, $_{67}\text{Ho}$, $_{68}\text{Er}$, $_{69}\text{Tm}$; and again to decrease the abundances of the heaviest members, $_{70}\text{Yb}$ and $_{71}\text{Lu}$. There is thus a very interesting correlation between the origin of the nuclides and the smoothing operation performed by SUESS and UREY. To a first approximation they have decreased the abundances of the *s*-process nuclides and increased the

* It was pointed out by TAYLOR and AHRENS (1959) that the solar system elemental K/Rb ratio of 220 may be unique since the K isotopes are produced mainly by the *s*-process and the Rb isotopes mainly by the *r*-process.

abundances of the r -process nuclides. It may be seen from Fig. 2 that the rare earth elements La, Ce, Pr and Nd are formed almost exclusively by the s -process; Sm and Eu by both s - and r -processes; Gd, Tb, Dy, Ho, Er and Tm predominantly by the r -process and Yb and Lu by a combination of s - and r -processes. Minor contributions from the p -process occur for La, Ce, Sm, Gd, Dy, Er, Yb and Lu. Minor contributions from the s -process occur for Gd and Dy. The details may be seen in Table 2 and Figs. 2, 3 and 4.

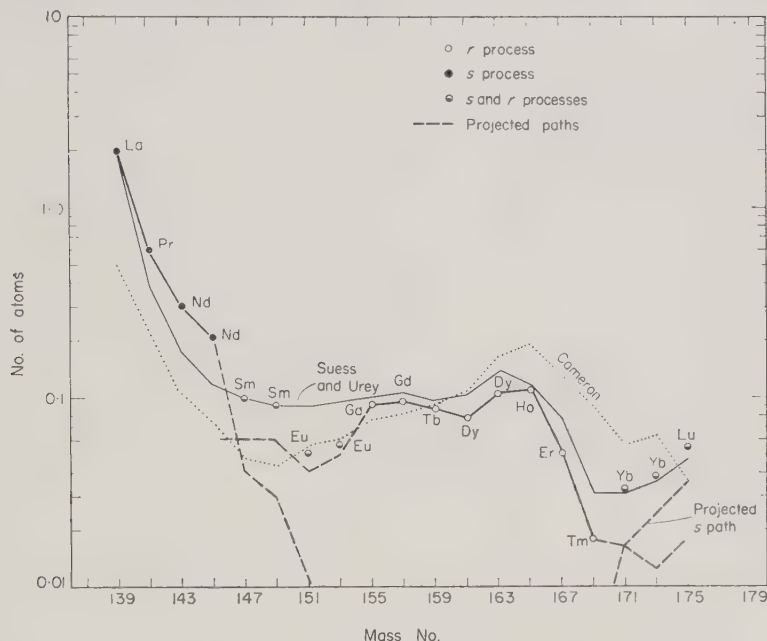


Fig. 2. Abundance of nuclides of odd mass number (A) from MINAMI (1935) plotted on a logarithmic scale against mass number. His data are recalculated relative to $\text{La} = 2.00$ atoms. (Suess and Urey (1956) set the abundance of La at 2.00 atoms. CAMERON (1959b) places the abundance of La at 0.500 atoms). Nuclides formed by the s -process are indicated by filled circles, those formed by the r -process by open circles, and those formed partly by each process by half-filled circles. Nuclides formed by the same process are joined. The abundance curves from SUSS and UREY (1956) and CAMERON (1959b) are shown for comparison. Their unaltered data are plotted.

It is apparent that the abundance of the odd- A isotopes (Fig. 2) does not reflect any simple relationship, but is a composite curve which, to begin with, shows a steady drop as the s -process nuclide abundances decline; followed by a trough at Eu^{151} where both s - and r -processes are at a minimum; followed by a rise to Dy^{163} and Ho^{165} due to the r -process; then a steep descent to Tm^{169} followed by a rise to Lu^{175} as the s -process again makes a contribution. The projected paths of the r - and s -processes are sketched to indicate this effect; no quantitative significance should be attached to these. On the basis of the Minami data, the low abundances of Eu^{159} , Eu^{163} and Tm^{159} are a consequence of the trough between the s -process peak at La^{139} and the r -process peak at Dy^{163} or Ho^{165} . An attempt to put a smooth curve through this data will depress the s -process abundances and elevate the r -process abundances as SUSS and UREY have done, and as is apparent

Table 2. Abundance of La, Ce and Nd in igneous rocks

<i>Z</i>	Element	* p.p.m. by wt.	* Nos. of atoms	† p.p.m. by wt.	† Nos. of atoms	‡ p.p.m. by wt.	‡ Nos. of atoms	§ Nos. of atoms
57	La	100	1.00	200	1.00	30	1.00	1.00
58	Ce	200	1.98	600	2.97	70	2.31	5.78
60	Nd	50	0.48	100	0.48	50	1.61	0.90

* CHODOS, G-1 granite (AHRENS and FLEISCHER, 1960).

† BERMAN (1957) G-1 granite.

‡ BERMAN (1957) W-1 diabase.

§ EDGE, thirteen granites (personal communication).

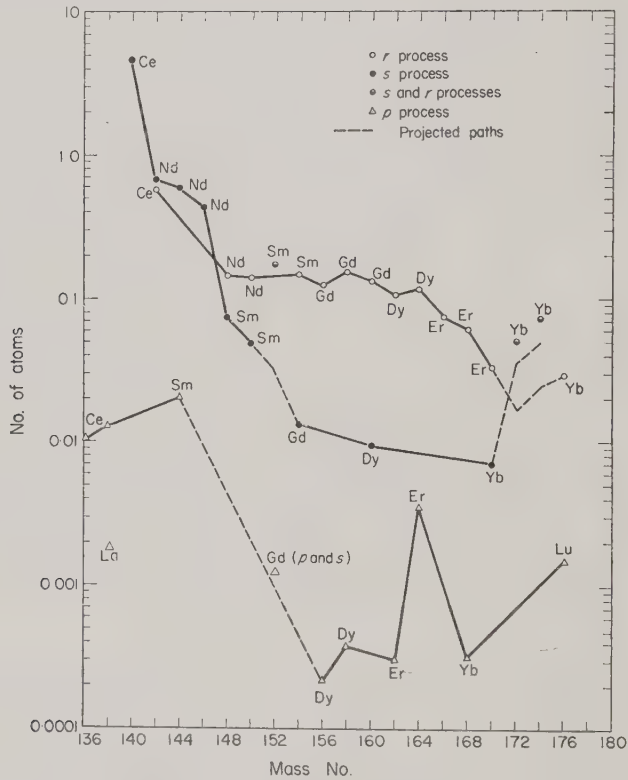


Fig. 3. Abundance of nuclides of even-*A* (from MINAMI (1935)) plotted on a logarithmic scale against *A*. *s*-, *p*- and *r*-process paths are indicated. Data are calculated relative to La = 2.00 atoms.

from Fig. 2. Thus, a smoothly varying abundance curve for the odd-*A* nuclides of the rare earths can only conceal significant irregularities.

In Fig. 3 the abundances of the even-*A* nuclides are plotted from the data given by MINAMI (1935). Fig. 4 shows the abundances of the even-*A* isobars from MINAMI (1935), SUESS and UREY (1956) and CAMERON (1959b).

Ce^{140} should be expected to be inherently more abundant than the other even- A rare earth nuclides, because of the magic number effect at $N=82$. This effect is brought out very clearly in Fig. 18 of AHRENS (1957, p.22).

The abundance pattern is not seriously disturbed by the several radioactive rare earth nuclides. La^{138} , Ce^{142} , Nd^{144} , Sm^{147} and Lu^{176} are all radioactive but with very long half lives, so that little relative change has been produced in the abundances. Sm^{147} has the shortest half life ($t_{\frac{1}{2}} = 1.3 \times 10^{10}$ years) and is the

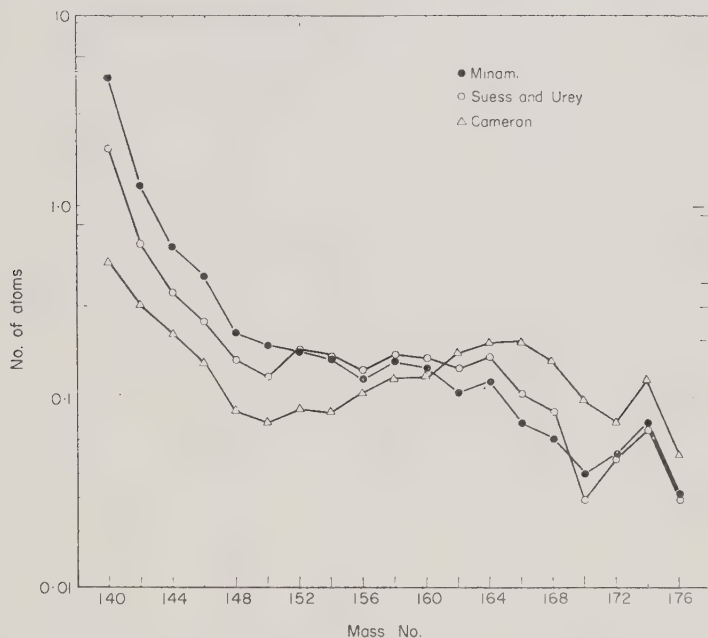


Fig. 4. Abundances of the even- A isobars plotted on a logarithmic scale against mass number (A). Data from MINAMI (1935) (calculated relative to $\text{La} = 2.00$ atoms), SUESS and UREY (1956) and CAMERON (1959b). Note that Ce^{136} and Ce^{138} are not included.

most abundant of the naturally occurring radioactive nuclides. However, it would have been only slightly more abundant 4.5×10^9 years ago at the time of condensation of the solar system (the figure is 1.27 atoms at 4.5×10^9 years ago for each atom at present).

CAMERON (1959b) has used NODDACK's data as a basis for his rare earth abundances. He has taken the abundance of La^{139} as 0.500 atoms. Although he uses the same abundance as SUESS and UREY (1956) for Ba^{138} (2.622 atoms) he has set the La^{139} abundance at about one-fifth of this to reflect the factor of about 5 between their respective 25-keV neutron-capture cross-sections. His data are plotted in Figs. 2 and 4. The Ce/Nd ratio is 0.658 , and, compared with SUESS and UREY figures, the relative abundances of the heavier nuclides are very much higher, with a well defined peak at $A=165$. This results from fission products derived by fission following β -decay from a postulated abundance peak on the rapid capture path at Pb^{266} (with a hypothetical closed shell involving 184

Table 3. Abundances, as numbers of atoms of the individual nuclides, calculated from MINAMI's (1935) results and expressed relative to $\text{La} = 2.00$

<i>Z</i>		Element abundance	<i>A</i>	Nos. of atoms	Process of* formation
57	La	2.00	138	0.00178	<i>p</i>
			139	1.998	<i>s(m)</i>
58	Ce	5.19	136	0.010	<i>p</i>
			138	0.0130	<i>p</i>
			140	4.592	<i>s(m)</i>
			142	0.575	<i>r</i> only
59	Pr	0.599	141	0.599	<i>s(m)</i>
60	Nd	2.48	142	0.673	<i>s</i> only (<i>m</i>)
			143	0.303	<i>s</i>
			144	0.592	<i>s</i>
			145	0.206	<i>s</i>
			146	0.426	<i>s</i>
			148	0.141	<i>r</i> only
			150	0.139	<i>r</i> only
61	Pm	—			
62	Sm	0.647	144	0.0204	<i>p(m)</i>
			147	0.0975	<i>rs</i>
			148	0.0729	<i>s</i> only
			149	0.0895	<i>rs</i>
			150	0.0483	<i>s</i> only
			152	0.172	<i>rs</i>
			154	0.146	<i>r</i> only
63	Eu	0.105	151	0.0502	<i>rs</i>
			153	0.0548	<i>rs</i>
64	Gd	0.608	152	0.00122	<i>ps</i>
			154	0.0131	<i>s</i> only
			155	0.0896	<i>r</i>
			156	0.124	<i>r</i>
			157	0.0953	<i>r</i>
			158	0.151	<i>r</i>
			160	0.133	<i>r</i> only
65	Tb	0.0862	159	0.0862	<i>r</i>
66	Dy	0.414	156	0.000217	<i>p</i>
			158	0.000373	<i>p</i>
			160	0.00950	<i>s</i> only
			161	0.0782	<i>r</i>

* BURBIDGE *et al.* (1957).

Table 3—*continued*

<i>Z</i>		Element abundance	<i>A</i>	Nos. of atoms	Process of formation
67	Ho	0.110	162	0.106	<i>r</i>
			163	0.103	<i>r</i>
			164	0.117	<i>r</i>
			165	0.110	<i>r</i>
68	Er	0.223	162	0.000303	<i>p</i>
			164	0.00348	<i>p?</i>
			166	0.0745	<i>r</i>
			167	0.0512	<i>r</i>
			168	0.0604	<i>r</i>
			170	0.0332	<i>r</i> only
69	Tm	0.0177	169	0.0177	<i>r</i>
70	Yb	0.232	168	0.000325	<i>p</i>
			170	0.00703	<i>s</i>
			171	0.0332	<i>s = r</i>
			172	0.0506	<i>sr</i>
			173	0.0374	<i>sr</i>
			174	0.0739	<i>sr</i>
			176	0.0295	<i>r</i> only
71	Lu	0.0567	175	0.0552	<i>sr</i>
			176	0.00147	<i>p</i>

neutrons). These events do not occur in the BURBIDGE scheme, in which spontaneous fission occurs at about $A = 260$. The author is not competent to discuss the nuclear physics involved but notes that "These difficulties arise because of the difficulty of extrapolating fission systematics into the very heavy element region" (CAMERON, 1959a, p.215).

As was stated in the last section, certain difficulties arise from the use by CAMERON of NODDACK's data. If the chondrites possess this type of abundance pattern, then it seems that a major fractionation has occurred between chondrites and the earth. This is not observed for other elements and in particular for the K/Rb ratio, the closest well authenticated analogy.

SUESS and UREY (1956, p.67) state, "The rare earth elements have chemical properties so similar that any major separation of these elements from each other seems to be improbable in any kind of cosmochemical process." If this view is accepted, the corroborative evidence of other workers which supports the MINAMI abundances must lead to the acceptance of the same relative abundances for chondrites.

The fruitful suggestion by UREY (1952) that the chondrites are the best average sample of the non-volatile elements in the solar system was based on the

Table 4. Sum of even- A isobars

A	*	†	‡
136	0.0100	0.0044	0.00112
138	0.0148	0.00746	0.00189
140	4.592	2.00	0.509
142	1.248	0.640	0.301
144	0.612	0.3548	0.213
146	0.426	0.248	0.150
148	0.214	0.157	0.0856
150	0.187	0.130	0.0738
152	0.173	0.177	0.0867
154	0.159	0.165	0.0837
156	0.124	0.141	0.106
158	0.151	0.170	0.129
160	0.143	0.162	0.128
162	0.106	0.142	0.171
164	0.121	0.162	0.197
166	0.0745	0.104	0.192
168	0.0607	0.0853	0.157
170	0.0402	0.0295	0.0974
172	0.0506	0.0480	0.0750
174	0.0739	0.0678	0.125
176	0.0310	0.0291	0.0509

* MINAMI's data from Table 3 of this paper.

† SUESS and UREY (1956, Table 3).

‡ CAMERON (1959b, Table 1).

idea that they represent a "heterogeneous mixture of materials from many sources" (SUESS and UREY, 1956, p. 54). Although they are probably the least differentiated sample to which we have access, it should be remembered that some workers (e.g. RINGWOOD, 1959) believe that the chondrites are not a primitive mixture, but have originated in a planet during a partial reduction process.

Table 5. Comparison of europium abundances

Source	Eu relative to Si = 10^6 atoms
NODDACK (1935)	0.25
SUESS and UREY (1956)	0.187
CAMERON (1959b)	0.115
BATE <i>et al.</i> (1960)	0.078
MINAMI (1935)*	0.105

* From Tables 1 and 3 of this paper. This is a relative abundance based on La = 2.00 atoms.

THE ABUNDANCE OF EUROPIUM

The abundance of europium in chondrites was given by NODDACK (1935) as 0.25 p.p.m. BATE *et al.*, (1960) have determined Eu in chondrites by neutron activation analysis. Their average for five samples is 0.078 ± 0.003 p.p.m. which is over three times lower than NODDACK's figure. The abundance of Eu in numbers of atoms relative to Si = 10^6 atoms is, by coincidence, 0.078. In Table 5, the abundances of Eu from different sources are compared. CAMERON's abundance (0.115) is close to the experimental figure. The value derived in this paper from MINAMI's data, recalculated to a basis of La = 2.00 atoms (same base as SUESS and UREY) is 0.105, which is closer to the observed value. We can see from Fig. 2 that the higher value (0.187) of SUESS and UREY (1956) results from the smoothing process. An exact match with the Eu figure of BATE *et al.* is produced from MINAMI's data by lowering the abundance of La from 2.00 atoms to 1.65 atoms relative to Si = 10^6 . It is tentatively suggested that the data of BATE *et al.* provide some support for the conclusions of this paper.

An accurate determination of one other rare earth element, preferably several elements removed from Eu, would probably decide between the alternative abundance patterns in chondrites.

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Isotopic composition of lead in pegmatitic feldspars*

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Abstract—An ion-exchange method was developed for extracting microgram quantities of lead from pegmatitic feldspars. The isotopic composition of lead in feldspars ranging from 350 to 2750 million years (m.y.) in age was determined. Model ages were calculated and were generally found to be in good agreement with independent age determinations. The results are compatible with a lead model stipulating relatively short periods of time in a crustal environment for the lead.

In one instance where there was a large discrepancy between the model age and the known age, because of excess radiogenic lead in the feldspar, the anomaly was resolved by acid leach experiments which preferentially removed the excess radiogenic lead.

The lead content of twenty-five feldspars was measured and found to range from <20 p.p.m. to 500 p.p.m.

INTRODUCTION

THE time-dependent variations in the isotopic composition of lead, resulting from the radioactive decay of uranium and thorium, have been the subject of many investigations (see MARSHALL, 1957, for bibliography). For the most part these investigations have been confined to macroscopic lead minerals, primarily galena. Two important limitations arise in the interpretation of these data: first, the frequent inability to date galena-bearing deposits independently of the time-dependent lead isotope ratios and second, the considerable uncertainty which exists as to the exact origin of many of these deposits.

Lead is significantly enriched in many pegmatitic microclines; WEDEPOHL (1956) has found a range of 20–200 p.p.m. for such samples. On the other hand, the uranium and thorium content of feldspars is generally very low (PICIOTTO, 1950; TILTON *et al.*, 1955). Thus, in most cases, the ratio of lead to uranium and thorium is so high that the isotopic composition of the lead should remain unchanged subsequent to the formation of the feldspar. In this way, pegmatitic feldspars are similar to macroscopic lead minerals. However, in contrast to galena deposits, almost all geochronometric methods developed to date can be used to establish the age of pegmatites. Examples of such studies are found in ALDRICH *et al.* (1956), WETHERILL *et al.* (1956), WASSERBURG (1954) and GAST *et al.* (1958). Furthermore, these studies indicate that in many cases the absolute age can be determined on the microcline itself. Thus the time when the lead was deposited can be established quite independently of any knowledge of its isotopic composition. This presents an opportunity to study the lead isotope composition as a function of time.

Previous determinations of the isotopic composition of lead in feldspars are given by TILTON *et al.* (1955), ALDRICH *et al.* (1956) and KOUVO (1958). In the present work, lead isotope compositions for eleven feldspar samples ranging in age from 350 to 2750 m.y. have been determined.

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EXPERIMENTAL

Introduction

The experimental problem of measuring the isotopic composition of lead occurring in concentrations of less than 0.01 per cent is twofold: first, chemical techniques for separating microgram quantities of lead from rocks and minerals are needed and second, mass spectrometric techniques for the determination of isotope abundance ratios on small samples are required. Several procedures and techniques have been described by TILTON *et al.* (1956), ALDRICH *et al.* (1956), CHOW and MCKINNEY (1958) and MAYNES and MCBRYDE (1957).

Because of the ubiquitous occurrence of lead in ordinary C.P. reagents, considerable effort is required in purifying reagents and cleaning apparatus. It is clearly advantageous to minimize the number of reagents and the amount of apparatus.

The detailed studies of KRAUS and NELSON (1956) on the anion-exchange properties of a number of elements in various concentrations of HCl indicated the feasibility of separating lead by an ion-exchange method. A study of their results indicated that lead could readily be separated from all elements except silver by absorption on Dowex 1 from a 1 N HCl solution and desorption with 8 N HCl. In such a procedure, aside from the resin, only HCl and water are used in quantity.

Reagents and preparation

Deionized water was prepared by passing distilled water through Dowex 1-8% 100-200 mesh resin and then through Dowex 50-8% 100-200 mesh resin. It was collected and stored in polyethylene carboys. The deionized water was redistilled in a fused silica still and collected in polyethylene bottles. The lead content of water prepared in this way was <0.05 p.p.b.

Hydrochloric acid was prepared by passing anhydrous HCl through a saturated HCl solution to filter out any particulate matter, and then into purified water until the concentration reached 9 N. This acid was diluted with pure water to the desired concentrations. Lead content of the 9 N HCl was <1 p.p.b. Hydrofluoric acid was prepared in a similar way; its lead content was 0.8 p.p.b.

Perchloric acid was prepared by distilling reagent grade 70% HClO_4 twice in a fused silica still under reduced pressure.

Nitric acid was prepared by distilling reagent grade concentrated HNO_3 twice in a fused silica still under reduced pressure.

Ammonium hydroxide was prepared from anhydrous ammonia and pure water.

Anion resin—Analytical grade Dowex 1-8% 100-200 mesh* was used. No pretreatment was necessary.

A number of precautions were employed to minimize contamination from the apparatus used. All dissolutions and evaporations were carried out in Teflon beakers which were cleaned by immersion in hot concentrated HNO_3 for 12 hr or more. Glass columns and centrifuge tubes were cleaned by immersion for 12 hr or more in hot 3 N KOH followed by similar treatment in hot concentrated HNO_3 .

Procedure

A 0.9 cm $\times$ 28 cm column was prepared by settling a batch of resin through 1.0 N HCl. After settling, the column was washed with 5 column volumes of 1.0 N HCl. A small column (0.4 cm $\times$ 15 cm) was similarly prepared.

(1) The sample is powdered to <80 mesh with an agate mortar and pestle, washed in pure water and dried.

(2) From 0.5 to 4 g of sample is weighed into a 50 ml Teflon beaker. The sample is heated for several hours with several millilitres of HF and HClO_4 and finally evaporated to a wet mush of perchlorates.

(3) The perchlorates are dissolved in 60 ml of pure water and transferred to 50 ml centrifuge

* Obtained from Bio-Rad Laboratories, Berkeley, California.

tubes. Aluminium hydroxide is precipitated with anhydrous NH_3 and centrifuged. The centrate is discarded.

(4) The aluminium hydroxide is dissolved in a few millilitres of concentrated HCl, evaporated to dryness and taken up in 50 ml of 1.0 N HCl.

(5) The aluminium solution, containing lead and other minor elements, is passed through the 0.9×28 cm column. The flow rate is adjusted to 0.5 ml/min using a Teflon stopcock at the outlet of the column. The eluate is discarded.

(6) The column is eluted with 70 ml of 1.0 N HCl. The eluate is again discarded. Finally, the column is eluted with 35 ml of 8.0 N HCl. The eluate is discarded until the colour change in the resin (light yellow-orange) approaches to within 5 cm of the bottom of the column. The remaining 8.0 N HCl (containing the lead) is collected in a 30 ml Teflon beaker.

(7) The final eluate is evaporated to dryness and taken up in 6 ml of 1.0 N HCl.

(8) The 6 ml of solution is passed through the 0.4×15 cm column at a flow rate of 0.3 ml/min. The eluate is discarded.

(9) The column is eluted with 10 ml 1.0 N HCl which is discarded, and finally with 7 ml of 8.0 N HCl. The 8.0 N HCl eluate is discarded until the colour change in the resin approaches the bottom of the column after which the eluate (containing the lead) is collected in a 10 ml Teflon beaker.

(10) The solution is evaporated to dryness and converted to the nitrate by taking up in 1 ml concentrated HNO_3 and re-evaporating to dryness. The sample is then dissolved in 2 ml of 2% HNO_3 .

(11) The nitric acid solution is transferred to a 3 ml centrifuge tube and the pH is adjusted to 4.5 with NH_4OH . The solution is then heated in a water bath and PbS is precipitated by bubbling H_2S through the solution.

The most time-consuming steps in the above procedure are the sample dissolution, taking from 4 to 12 hr, and the ion-exchange separation, requiring ~ 8 hr (including both columns). Obviously, two or three samples can be processed simultaneously, reducing the time consumed per sample.

In several separations the lead was followed through the complete procedure by using a Pb^{210} tracer. The overall recovery was determined in three complete separations and ranged from 60 to 75 per cent. Both the coprecipitation with aluminium hydroxide and the ion-exchange separation gave recoveries greater than 95 per cent. Most of the loss probably occurs in the transfer of small amounts of solutions.

No detailed study of possible interfering ions was made. The behaviour of iron was semi-quantitatively determined by the colour of the ferric ion; no yellow colour was adsorbed from the 1.0 N HCl solution, indicating little or no adsorption of iron.

In order to test the above procedure on material other than feldspars a single separation of lead from a manganese nodule was attempted. A 1.0 g sample was decomposed in 6 N HCl, the insoluble fraction being discarded. The solution was evaporated to dryness, taken up in 30 ml 1.0 N HCl, and put through the procedure outlined above. A clean black precipitate of lead sulphide was obtained which gave excellent lead emission on the mass spectrometer. The work of GOLDBERG (1954) indicates significant concentrations of copper, nickel, iron and manganese in these nodules. Thus it can be inferred that ion-exchange separation procedure affords adequate separations from these elements.

Determination of lead in blanks

Lead concentrations in individual and overall reagent blanks were determined using a stable isotope tracer. ECKELMANN and KULP (1956) obtained gramme quantities of relatively pure Pb^{206} from a number of pitchblendes. Their most radiogenic lead sample, K-14, was used as a stable isotope tracer in this study. A solution with a lead concentration of $28.4 \mu\text{g/ml}$ was prepared gravimetrically. With a 2 ml aliquot ($56.8 \mu\text{g}$) of this solution, $0.1 \mu\text{g}$ of normal lead results in a 35 per cent change in the $\text{Pb}^{208}/\text{Pb}^{206}$ ratio.

Three separate overall reagent blank determinations were made. In addition to the usual reagents, 1.0 g of purified $\text{Al}(\text{Cl})_3$ was added as a carrier in the hydroxide precipitation step. The results are listed in Table 1. In the first determination all operations were done in the open

air; in the last two determinations evaporations were carried out in Teflon enclosures, preventing fall-in of dust from the atmosphere. The difference in the lead concentrations found suggests that measurable amounts of lead contamination can result from atmospheric dust. This is in agreement with the observations of CHOW and MCKINNEY (1958).

Table 1. Blanks

	Pb μg	Evaporation
(1)	0.37	Uncontrolled
(2)	0.042	Controlled
(3)	0.082	Controlled*

* The sample was accidentally left exposed in the hood for $1\frac{1}{2}$ hr.

Emission spectrography

The concentrations of lead in two feldspars, F-3 and COD-2, were determined using the stable isotope tracer. These two samples were then used as standards for emission spectrographic determinations of the lead content of other feldspars. A Jarrell Ash Model JA 7101 plane grating spectrometer was used, with an indium internal standard and Na_2CO_3 buffer. Possible errors range from 50 per cent (<30 p.p.m.) to 10 per cent (500 p.p.m.).

Uranium determination

A thick source α -scintillation counter, of the type described by KULP *et al.* (1952), was used to determine the α -activity of four feldspars. Samples were counted for at least 1000 counts so that the standard counting error was less than 3 per cent. A concentration of 1.0 p.p.m. uranium results in 40 counts/hr above background; since some of the α -activity may arise from thorium the estimated uranium contents are an upper limit. The background counting rate varied between 36 count/hr and 42 count/hr. The results are listed in Table 2.

Table 2. Alpha activity of feldspars

Sample	α -counts/hr above background	Equivalent p.p.m. U
Gm-YW-2	0	<0.1
F-3	4 ± 4	0.1 ± 0.1
Gm-YB-15	0	<0.1
F-15	$44 \pm$	1.0 ± 0.1
F-15 (leached)	0	<0.1

MASS SPECTROMETRY

Isotope abundance measurements were made on a direction focusing 60° sector field, 6 in. radius of curvature mass spectrometer. Defining slits of 0.004 in. and a collector slit of 0.010 in. were used. Resolution obtained using these parameters is seen in the spectrum shown in Fig. 1.

The surface ionization ion source used is similar to that described by ALDRICH *et al.* (1953). In order to avoid cross-contamination between samples, ion source parts exposed to the filament were washed in hot nitric acid between runs. From 10 to 20 μg of lead sulphide obtained in step

(11) of the chemical procedure were transferred to a 0.001 in. $\times$ 0.030 in. tantalum filament and heated to dryness, yielding a black or grey powder on the filament. The total current of Pb^+ ions obtained from the ion source ranged from 10^{-12} to 10^{-11} A.

Two different ion detection systems were employed in the course of the work. Most of the determinations were made with a sixteen-stage electron multiplier in conjunction with a vibrating

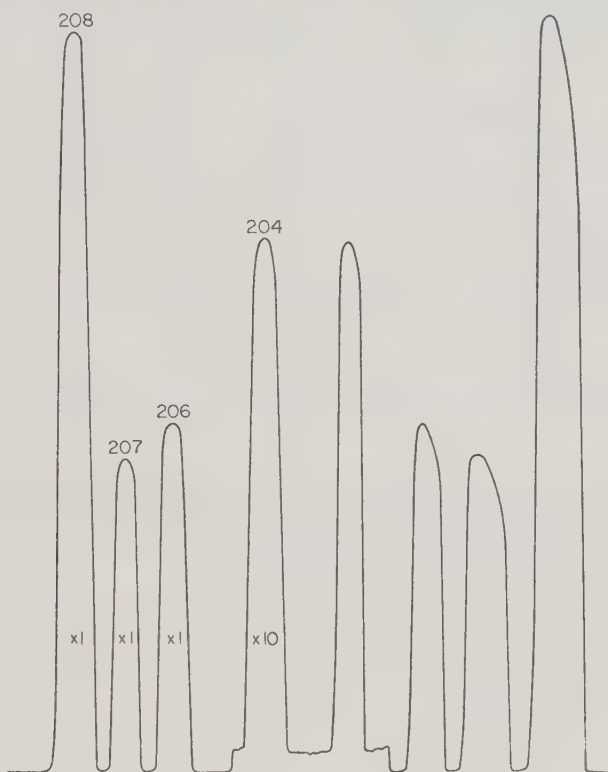


Fig. 1. Solid source lead spectrum.

reed electrometer. Subsequent studies indicated that the multiplier was not necessary and a number of determinations were made using a $4 \times 10^{10} \Omega$ input resistor on an Applied Physics vibrating reed electrometer.

The possibility of systematic discrimination in the electron multiplier was investigated by comparing lead isotope standards, which had previously been determined by the $\text{Pb}(\text{CH}_3)_4$ method without a multiplier, with both of the presently used methods. Comparison of all three methods is shown in Table 3. The runs in which the electron multiplier was used are shown

Table 3. Analyses of USGS Pb standard

	No. of runs	204	206	207	208
$\text{Pb}(\text{CH}_3)_4$	40	0.0613	1.00	0.955	2.23
PbS (no mult)	2	0.0616	1.00	0.956	2.24
Pbs (mult, no corr)	11	0.0624	1.00	0.949	2.20
PbS (mult, $\sqrt{m}$ corr)	11	0.0621	1.00	0.951	2.21

with and without the square-root-of-the-mass ratio correction (INGHRAM and HAYDEN, 1954). Although the difference is well within the estimated error, the corrected ratios are in somewhat better agreement with the runs employing no multiplier than the uncorrected ratios. All runs employing an electron multiplier are here reported with the correction.

No systematic study of the experimental uncertainty was made. The standard deviation of various ratios for individual runs is given in Table 4 as an indication of the quality of a particular run. Duplicate determinations and replicate runs on a single standard indicate a reproducibility of better than 2 per cent for all ratios and, in general, better than 1 per cent for the Pb^{207}/Pb^{206} ratio.

DESCRIPTION AND LOCATION OF SAMPLES

Gm-YP-1: A pink microcline with fine exsolution lamellae (0.5 mm) and small intergrowths of quartz. The sample is from a small pegmatite which outcrops about 500 ft west of Cody Dam in Shoshone Gorge, Wyoming. The pegmatite has been described and dated (2720 m.y.) by GAST *et al.* (1958).

Gm-YB-12: A light pink microcline with fine exsolution lamellae taken from a zoned pegmatite near Christmas Lake in the Beartooth Mountains, Montana. The hand specimen shows a small amount of iron-oxide staining. The pegmatite has been dated (2750 m.y.) by GAST *et al.* (1958).

Gm-YB-15: A light pink microcline with moderate (0.75 mm) exsolution lamellae from a discordant pegmatite $\frac{1}{4}$ mile south of Blackstone Lake in the Beartooth Mountains, Montana. The hand specimen shows a small amount of iron-oxide staining. The pegmatite has been dated by GAST *et al.* (1958).

F-7: A very light green microcline with coarse (~ 1 mm) exsolution lamellae from a small pegmatite intruding "black schist" 0.8 miles south of Glendale, South Dakota. The sample was taken from an outcrop on the east side of the road connecting Spokane and Keystone. The hand specimen contains abundant iron-oxide stains along cleavage cracks. The pegmatite is believed to be of the same age as the Ingersoll pegmatite (see below).

Gm-DA-2: A light tan-grey microcline with coarse exsolution lamellae. The sample is from the Tin Mountain pegmatite near Custer, South Dakota. The hand specimen shows a small amount of clay alteration and iron-oxide staining. The pegmatite is believed to be of the same age as the Ingersoll pegmatite (see below).

Gm-COD-2: A green microcline with fine exsolution lamellae from a small pegmatite located midway between West Creek and Crystal Peak, near Flourissant, Colorado. The hand specimen showed surficial weathering with abundant iron-oxide staining and a few manganese-oxide dendrites. The 1070 m.y. age quoted in Table 4 is that of the adjacent Pikes Peak granite as determined by ALDRICH *et al.* (1958).

F-8: A green microcline with no macroscopic exsolution lamellae. The sample was taken from an amazonite pegmatite in Tordal, Norway described by OFTEDAL (1942).

Gm-V-1: A deep-green amazonite from the Morefield pegmatite, Amelia Courthouse, Virginia. The hand specimen showed no exsolution lamellae and no alteration.

Gm-YW-2: A white microcline with moderate exsolution lamellae and large quartz intergrowths. The sample is from a small microcline-quartz pegmatite located on the southern slope of the Bridger Mountains, approximately 12 miles north of Bonneville, Wyoming. The hand specimen showed abundant iron-oxide staining. The sample gave a Rb-Sr age of 2600 m.y. (P. W. GAST, unpublished).

F-3: A white microcline with moderate exsolution lamellae. The sample was taken from pit no. 2 in the Bob Ingersoll pegmatite, Keystone, South Dakota. The most likely age of this pegmatite is 1600 m.y. (WETHERILL *et al.*, 1956).

F-15: A cleavelandite from pit no. 2 in the Bob Ingersoll pegmatite, Keystone, South Dakota.

RESULTS

Eleven pegmatitic feldspars were investigated. The lead isotope composition and lead content of these samples are given in Table 4. In addition to the feldspars, the lead isotope composition in a single manganese nodule is shown. The nodule is from the North Atlantic and

Isotopic composition of lead in pegmatitic feldspars

Locality	Pb	F^{207}/F^{206}	F^{207}/F^{208}	F^{207}/F^{206}	F^{208}/F^{206}	F^{207}/F^{208}	F^{206}/F^{207}	(m.y.)	Age (m.y.)
Gm-YP-1 Shoshone Canyon, Cody, Wyoming	100	0.0722 ± 0.0011	1.087 ± 0.006	2.460 ± 0.014	13.84 ± 0.21	15.02 ± 0.22	34.00 ± 0.57	2850 ± 200	2720
Gm-YB-12 Christmas Lake Pegmatite Beartooth Range, Montana	55	0.0708 ± 0.0011	1.062 ± 0.010	2.383 ± 0.020	14.11 ± 0.22	14.99 ± 0.22	33.66 ± 0.45	2700 ± 200	2750
Gm-YB-15 Blackstone Lake Pegmatite Beartooth Range, Montana	25	0.0698 ± 0.008	1.050 ± 0.008	2.340 ± 0.022	14.31 ± 0.16	15.08 ± 0.19	33.77 ± 0.50	2600 ± 150	2750
F-7 Glendale Pegmatite Black Hills, S. Dakota	390	0.0618 ± 0.0007	0.959 ± 0.008	2.212 ± 0.017	16.18 ± 0.18	15.51 ± 0.12	35.81 ± 0.34	1550 ± 125	1600
Gm-DA 2 Tin Mountain Black Hills, S. Dakota	88	0.0616 ± 0.0004	0.955 ± 0.006	2.216 ± 0.011	16.23 ± 0.10	15.50 ± 0.14	35.89 ± 0.19	1500 ± 150	1600
Gm-COD-2 Crystal Peak Peg- matite Pikes Peak, Colorado	495*	0.0610 ± 0.0010	0.923 ± 0.008	2.192 ± 0.021	16.64 ± 0.28	15.35 ± 0.26	36.58 ± 0.51	1050 ± 200	1070
F-8 Tardol, Norway (1) (2)	240	0.0573 ± 0.0004 0.0574 ± 0.0005	0.895 ± 0.006 0.896 ± 0.008	2.124 ± 0.011 2.134 ± 0.015	17.45 ± 0.12 17.42 ± 0.15	15.61 ± 0.11 15.62 ± 0.12	37.12 ± 0.27 37.19 ± 0.34	750 ± 150 750 ± 150	950
Gm-V-1 Morsefield Pegmatite Anelia Courthouse, Virginia	435	0.0550 ± 0.0007	0.862 ± 0.008	2.110 ± 0.014	18.17 ± 0.23	15.63 ± 0.19	38.39 ± 0.44	200 ± 200	(350)
Gm-YW. 2 Bonneville, Wyoming	60	0.0602 ± 0.0007	0.939 ± 0.006	2.070 ± 0.014	16.61 ± 0.19	15.61 ± 0.17	34.45 ± 0.47	1350 ± 150	2600
F-3 Bob Ingersoll Peg- matite (1)† Black Hills, S. Dakota (2)	40*	0.0604 ± 0.0012 0.0598 ± 0.0004	0.928 ± 0.010 0.934 ± 0.009	2.112 ± 0.023 2.143 ± 0.017	16.55 ± 0.33 16.72 ± 0.11	15.47 ± 0.33 15.64 ± 0.16	35.18 ± 0.77 35.94 ± 0.32	1250 ± 300 1300 ± 150	1600
F-15 Ingersoll Cleave- landite	20	0.0548 ± 0.0005	0.860 ± 0.006	1.982 ± 0.013	18.25 ± 0.17	15.70 ± 0.12	36.14 ± 0.26		
Mn Nodule		0.0529 ± 0.0003	0.829 ± 0.888	2.079 ± 0.022	18.91 ± 0.28	15.69 ± 0.25	39.34 ± 0.48		

* By isotope dilution. † This sample was not washed in pure water before treatment.

its lead isotope composition is in good agreement with the results reported by CHOW and PATTERSON (1957).

The uranium content of several samples (Table 2) was found to be generally less than 0.1 p.p.m. Cleavelandite from the Bob Ingersoll pegmatite (F-15) was the only sample which contained measurable radio-activity and even this activity was readily leached out with warm 50% HNO_3 (15 min bath).

Four samples, Gm-YW-2, F-3, F-8 and F-15 originally gave anomalous model ages. In order to test the possibility of surficial contamination by more-radiogenic lead the anomalous samples were subjected to acid leach tests. The results of these tests are shown in Table 5. In

Table 5. Results of acid leach experiments

	$\text{Pb}^{206}/\text{Pb}^{204}$	$\text{Pb}^{207}/\text{Pb}^{204}$	$\text{Pb}^{208}/\text{Pb}^{204}$	Model age (m.y.)
<i>A. Bonneville Feldspar</i> (Gm-YW-2)				
1. Unwashed sample	16.61 ± 0.19	15.60 ± 0.17	34.38 ± 0.35	1350
2. Leached with 20% HNO_3 (10 min)	15.51 ± 0.17	15.29 ± 0.16	33.92 ± 0.34	1800
3. (a) Leached with 50% HNO_3 (15 min)	14.56 ± 0.14	15.26 ± 0.13	34.11 ± 0.43	2550 ± 100
(b) Leach solution	46 ± 4	20 ± 2	39 ± 4	
4. Releach of 3a with 50% HNO_3 (15 min)	14.69 ± 0.12	15.28 ± 0.15	34.36 ± 0.28	2500 ± 150
<i>B. Ingersoll Microcline</i> (F-3)				
1. Unwashed sample	16.55 ± 0.33	15.47 ± 0.33	35.18 ± 0.77	1250 ± 300
2. Washed in pure water	16.72 ± 0.11	15.64 ± 0.16	35.94 ± 0.32	1300 ± 150
3. Leached with 50% HNO_3 (15 min)	16.75 ± 0.17	15.72 ± 0.15	36.50 ± 0.66	1300 ± 150
<i>C. Ingersoll Cleavelandite</i> (F-15)				
1. Washed sample	18.25 ± 0.17	15.70 ± 0.12	36.14 ± 0.26	225 ± 150
2. Leached with 50% HNO_3 (15 min)	17.04 ± 0.17	15.65 ± 0.15	35.97 ± 0.30	1100 ± 200
<i>D. Tordal Microcline</i> (F-8)				
1. Washed sample	17.45 ± 0.12	15.61 ± 0.11	37.12 ± 0.27	750 ± 150
	17.42 ± 0.15	15.62 ± 0.12	37.19 ± 0.34	750 ± 150
2. Leached with 50% HNO_3 (15 min)	17.24 ± 0.15	15.41 ± 0.14	36.97 ± 0.40	700 ± 175

the case of Gm-YW-2 a pronounced change was found after a 10 min washing with 20% HNO_3 and an even greater change occurred during a 15 min washing with 50% HNO_3 . The isotopic composition of the lead in the leach solution was also measured and substantiates the fact that the readily soluble lead is highly radiogenic. Further leaching of the residue from the 50% HNO_3 wash resulted in no change. Similar experiments with the Bob Ingersoll microcline (F-3) and the Tordal microcline (F-8) caused no significant change in the isotopic composition of the lead.

The excess radiogenic lead in the cleavelandite sample (F-15) from the Bob Ingersoll pegmatite was probably due to the presence of microscopic plates of microlite which have been recognized in other hand specimens from the area and whose presence in this sample was indicated by the α -activity of the sample. The acid-leach experiment removed the α -activity and most of the excess radiogenic lead, but the sample is still somewhat anomalous; the degree of anomaly is comparable with that of the Ingersoll microcline (F-3) which was taken from the same location.

Results of the measurements of the lead content of twenty-five pegmatitic feldspars gave a range of from less than 20 p.p.m. to 500 p.p.m. The amazonites or green microclines all contained high amounts of lead (≥ 200 p.p.m.), but the lead content does not correlate with the intensity of green coloration. The highest concentration of lead, 500 p.p.m., was found in a pure white feldspar.

DISCUSSION

The isotopic composition of lead is a function of the U/Pb ratio of the past environments of the lead and the time spent in the various environments. The information derived from this study will therefore be in terms of these two parameters. The new measurements presented here allow a comparison of the history of lead in pegmatite feldspars with lead in macroscopic lead minerals. The data from macroscopic lead minerals have been analysed by a number of authors: HOLMES (1956), EBERHARDT *et al.* (1955), RUSSELL *et al.* (1954), VINOGRADOV (1955), TUGARINOV (1954) and others. The fundamental concepts which are used in almost all treatments of the time-dependent lead isotope variations were independently suggested by GERLING (1942), HOLMES (1946) and HOUTERMANS (1947), in their treatment of the first lead isotope determinations made by NIER (1938). The concepts are: (1) At the time the earth was formed, lead everywhere in the earth had the same isotopic composition; (2) There were small spatial variations in the U/Pb ratio; and (3) Both the inhomogeneities in the U/Pb ratio and the subsequent inhomogeneities in the lead isotope ratios are maintained.

The existence of so-called anomalous leads indicates quite clearly that the model based on these assumptions is not adequate for all lead samples. Using a development of the assumptions first suggested by HOUTERMANS and later developed by GEISS (1954) and EBERHARDT *et al.* (1955), BATE *et al.* (1960) suggest that the basic models can be retained if the isotopic composition of a lead sample is thought of as arising from two environments: the first being essentially that described by the GERLING-HOLMES-HOUTERMANS model, and the second, an environment with more variable U/Pb ratios. More concretely, it is suggested by BATE *et al.* that the history of a lead sample consists of a mantle history and a crustal history. The extent to which either of the two environments is significant depends on the length of time spent in each environment.

A graphical comparison of the isotopic composition of feldspar lead and lead from hydrothermal galenas is shown in Fig. 2. The statements (1), (2) and (3), given above, are assumed for this model; the initial lead isotope composition is taken as that of lead in meteoritic troilite nodules ($\text{Pb}^{206}/\text{Pb}^{204} = 9.50$, $\text{Pb}^{207}/\text{Pb}^{204} = 10.36$ and $\text{Pb}^{208}/\text{Pb}^{204} = 29.49$, PATTERSON, 1955). An age of 4550 m.y. is used. This is primarily the assumption that the earth was formed at the time when meteoritic materials were segregated into the different phases now observed. Lead development lines for present day $\text{U}^{238}/\text{Pb}^{204}$ atom ratios of 8, 9 and 10 are

shown. Isotopic compositions for over 150 galena samples are shown. These are taken from work done in the Department of Geophysics, University of Toronto and from analyses made at the Lamont Geological Observatory. The galena data are given mainly as a comparison and are discussed more fully in another paper

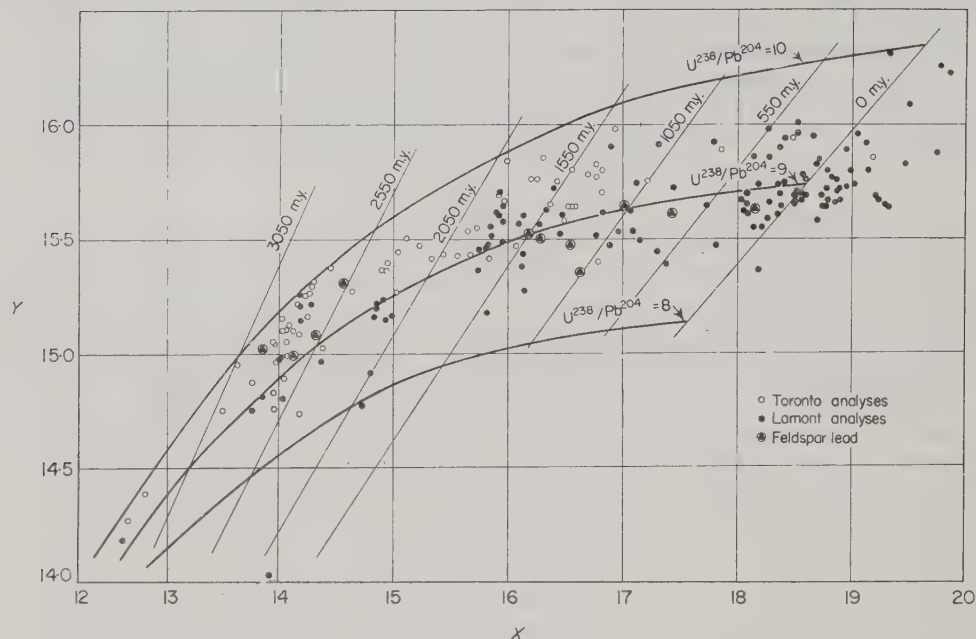


Fig. 2. Isochron plot of Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios from lead minerals.

(BATE *et al.*, 1960). Finally, the Pb^{206}/Pb^{204} and Pb^{207}/Pb^{204} ratios for the feldspar samples studied here are shown. Model ages given in column 8 of Table 4 and in Table 5 were derived from this plot.

As suggested earlier, deviations from the simple lead model can be formally explained by assuming that the isotopic compositions seen today are the result of the lead having spent time in different environments, i.e. the mantle and the crust. Thus any lead which had an extensive crustal history prior to its incorporation in a feldspar or galena crystal would yield a model age different from the true age. The degree of error would depend on the difference in the U/Pb ratio of the two environments and on the length of time spent in the second environment. The value of the parameter, U^{238}/Pb^{204} , for crustal rocks has not been studied very extensively. For accurate determinations of this ratio, the isotopic composition of the lead as well as the total lead and uranium contents must be known. The number of rocks for which this ratio has been determined is very limited. Table 6 summarizes most of the available data. The average value of the U^{238}/Pb^{204} ratio would appear to be somewhat higher in the upper crust than in the mantle. The range observed in the crust is certainly very much wider than the apparent range for the source of the galena lead.

It seems likely that most of the lead in pegmatites is derived from within the

crust. The material in metamorphic pegmatites such as the Beartooth pegmatites (samples Gm-YB-12 and Gm-YB-15) and the Shoshone Gorge pegmatite is probably derived from the local surroundings. The Pikes Peak and Black Hills pegmatites are associated with large granite intrusions; they may be differentiates of these

Table 6. Observed U^{238}/Pb^{204} for crustal rocks

	U^{238}/Pb^{204}	U (p.p.m.)	Pb (p.p.m.)
Pitkeranta granite*	23.3	7.5	27
Essonville granite†	22.0	2.74	93
Altai granodiorite*	15.5	2	8
Woodson Mt. granodiorite‡	14.3	—	—
Rubidoux leucogranite‡	44	—	—
Hawaiian Basalt§	12.3	0.5	2.6

* VINOGRADOV and ZYKOV (1955).

† TILTON *et al.* (1955).

‡ PATTERSON, SILVER and MCKINNEY (1956).

§ TILTON *et al.* (1954).

intrusions. Although the exact nature of the previous environment of the lead in these pegmatites is much in doubt, it seems reasonable to expect that it was in the crust. Because of the variability of the U/Pb ratio in crustal rocks some deviations from the model may be expected for the pegmatitic lead samples.

Seven of the ten pegmatites studied here yield model ages consistent with their known ages. The remaining three give model ages younger than those measured by direct methods. One of these, Bonneville (Gm-YW-2), gave a consistent lead isotope age after the sample was leached with nitric acid, but the other two localities, Ingersoll and Tordal remained inconsistent even after a similar acid treatment.

Age determinations were made on the microcline and on a lepidolite sample from the Tordal pegmatite. The results are given in Table 7. The striking discordance indicates that the history of this pegmatite is not simple and it is therefore difficult to establish the significance of the different ages without a more thorough study of the pegmatite.

The model ages of the cleavelandite and microcline from the Ingersoll pegmatite appear to be too young. Since there was some radioactivity in the cleavelandite its anomaly may not be significant. The anomaly in the microcline model age is small and may simply be an indication that the U^{238}/Pb^{204} ratio in the pre-crystallization crustal environment of this particular lead sample was somewhat higher than that of the neighbouring Glendale and Tin Mountain lead samples.

The question whether or not the isotopic composition which is measured can result partly from contamination subsequent to the incorporation of the original lead within the feldspar must be answered. The different results of acid leaching experiments on the Bonneville (Gm-YW-2), Ingersoll (F-3), and Tordal (F-8) microclines (Table 5) indicate that isotopically different types of lead exist in the Bonneville sample but not in the Ingersoll and Tordal samples. The data on the

Ingersoll cleavelandite (F-15) are not significant in this regard, since the excess radiogenic lead is readily explained as arising from uranium in the sample, probably in the form of microcline.

The differential leachability and the absence of radioactivity in the Bonneville sample suggest that the excess radiogenic lead was incorporated into the feldspar subsequent to its crystallization. This hypothesis of later addition is also supported

Table 7. Age determination on tordal pegmatite, Norway

Sample	Sr (p.p.m.) (normal)	Sr ^{87*} (p.p.m.)	Rb (p.p.m.)	Sr ⁸⁷ */Rb ⁸⁷	Rb/Sr age (m.y.)
A. Lepidolite Microcline (F-8)	<0.04 1.115	77.96 32.1	12,660 8552	0.0217 0.01337	1550 951
	K (%)	A ^{40*} (p.p.m.)	A ⁴⁰ */ Total A.	A ⁴⁰ */ K ⁴⁰	K/A age (m.y.)
B. Lepidolite	6.80	0.642	0.888	0.1130	1320
	Pb ²⁰⁶ /Pb ²⁰⁴		Pb ²⁰⁷ /Pb ²⁰⁴		Model age (m.y.)
C. Microcline (F-8)					
washed	17.45		15.61		750
	17.42		15.62		750
leached	17.24		15.41		700

* Indicates radiogenic component.

by the Pb²⁰⁷/Pb²⁰⁶ ratio of the excess radiogenic lead. The exact source of this lead is hard to define. It is suggested that the introduction of the lead may be related to later plutonic activity in adjacent areas.

In conclusion, it appears that in most cases the isotopic compositions of leads in pegmatitic microclines yield model ages consistent with true ages. Anomalous results, such as the Ingersoll microcline, are explained by the fact that lead in many pegmatites has a definite crustal history and must show variations from the model because the assumptions made for the model probably do not apply to the crust of the earth. The apparent infrequentness of anomalous feldspars is due to the fact that only long-term crustal histories in conjunction with large U²³⁸/Pb²⁰⁴ changes can yield discrepancies which are outside the experimental error.

The similarity between the microclines and normal ores (i.e. non-anomalous) ores, with respect to the model, indicates the possibility of similar environmental histories for the two types of minerals and, by analogy with the microclines, suggests that ore lead may have spent a relatively short period of time in a crustal environment before being incorporated into macroscopic lead minerals.

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The silica and alumina content of the standard rocks G-1 and W-1

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Abstract—In a review of some recent determinations of alumina and silica in the two standard rocks G-1 and W-1 it is shown that some of the values reported for these oxides agree closely with revised values calculated from the original data for these rocks and for a haplogranite glass.

INTRODUCTION

IN a number of recent publications (FAIRBAIRN *et al.*, 1951; SCHLECHT, 1951; FAIRBAIRN and SCHAIRER, 1952; FAIRBAIRN, 1953) the precision and accuracy of rock analysis by chemical methods has been considered. In the last of these papers FAIRBAIRN has shown that a systematic error exists in the results reported for the haplogranite glass and probably also for the two standard rocks G-1 and W-1. The discrepancies reported for the silica and alumina are of opposite sign and of the same order of magnitude, suggesting that the error arises by counting a small part of the silica as alumina.

CALCULATION OF THE ERROR INVOLVED IN DETERMINING SILICA AND ALUMINA

As the composition of the glass is known to within relatively narrow limits, the error involved in determining silica and alumina in this material can easily be calculated. Assuming that similar errors are involved in the determination of these elements in G-1 and W-1, a correction can be applied and "preferred values" calculated. Using this method FAIRBAIRN (1953) obtained values of 72.86% SiO_2 , 13.94% Al_2O_3 in G-1 and 52.69% SiO_2 14.72% Al_2O_3 in W-1. More recent photometric determinations of these elements by SHAPIRO and BRANNOCK (1956) and RILEY (1958) do not agree with the preferred values of FAIRBAIRN, nor do recent determinations made by the writer using a combined gravimetric and photometric method for silica, and a gravimetric method for alumina (see below). The original data for these two rocks and the haplogranite glass have therefore been re-examined and new corrections for the silica and alumina values of G-1 and W-1 calculated.

In his computation FAIRBAIRN has included analyses additional to those published in the four papers noted above. As these were not available to the writer, the data used in the present calculations have been limited to those given in the four papers listed. By making appropriate selections of the data a number of revised values for the silica and alumina in these rocks can be calculated; revised values obtained by four such calculations are given in Table 1, and the methods used to calculate these values are outlined below. Little difference exists between the silica values obtained by the four methods which, for W-1 are in

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agreement with the preferred value of FAIRBAIRN; for G-1 somewhat lower silica values were obtained. The agreement between the four alumina values is closer for G-1 than for W-1.

Method I. In this method the difference between the standard composition of the glass and the arithmetic mean of the results for it was used as a correction to be added (silica) or subtracted (alumina) from the arithmetic means of the thirty-four results for G-1 and thirty results for W-1 given by FAIRBAIRN *et al.* (1951).

Table 1. Revised values for the silica and alumina content of G-1 and W-1 (%)

	G-1		W-1	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
<i>Method I</i>				
arithmetic mean	72.24	14.34	52.33	15.17
correction	+0.41	-0.41	+0.41	-0.41
revised value	72.65	13.93	52.74	14.76
<i>Method II</i>				
arithmetic mean	72.27	14.30	52.38	15.04
correction	+0.32	-0.35	+0.32	-0.35
revised value	72.59	13.95	52.70	14.69
<i>Method III</i>				
arithmetic mean	72.34	14.40	52.42	15.21
correction	+0.41	-0.41	+0.41	-0.41
revised value	72.75	13.99	52.83	14.80
<i>Method IV</i>				
arithmetic mean	72.34	14.35	52.42	15.27
correction	+0.32	-0.35	+0.32	-0.35
revised value	72.66	14.00	52.74	14.92

This procedure gives values of 72.65% SiO₂, 13.93% Al₂O₃ in G-1 and 52.74% SiO₂, 14.76% Al₂O₃ in W-1.* This method of obtaining the revised values assumes that the performance of the analysts who undertook the examination of the glass was of the same overall standard as that of those who examined the standard rock samples.

Method II. As a refinement to *Method I*, values falling outside the range ($\bar{x} \pm 2s$) can be rejected, a device commonly used for the rejection of material in which more than normal experimental error occurs. The correction calculated from the results for the haplogranite glass is similarly recalculated following rejection of the results not in the range ($\bar{x} \pm 2s$). The revised values obtained are

* The corrections for silica and alumina for W-1 are not reduced in proportion to the silica content of FAIRBAIRN (1953).

72.59% SiO_2 , 13.95% Al_2O_3 in G-1 and 52.70% SiO_2 , 14.69% Al_2O_3 in W-1, values that do not differ significantly from those calculated by *Method I*.

Method III. As the names of the laboratories have been given, it is possible to select from the data for G-1 and W-1, results given by the laboratories that examined the glass. With one exception, the analysts involved in the eleven laboratories were the same for the glass as for the silicate rocks. By applying the correction to the data selected in this way, the following revised figures were obtained: 72.75% SiO_2 , 13.99% Al_2O_3 in G-1 and 52.83% SiO_2 , 14.80% Al_2O_3 in W-1.

Method IV. Calculation of the standard deviations for the silica values shows, however, that the performances in the analysis of the glass were not of the same standard as those of G-1 and W-1 by the same analysts. Thus for the glass, the standard deviation of the eleven results given for silica is 0.34 per cent, for the corresponding eleven results for G-1 it is 0.18 per cent and for the ten results for W-1 it is 0.16 per cent; compared with the standard deviation of 0.34 per cent for the thirty original determinations of silica in W-1, and 0.36 per cent for the thirty-four in G-1. Small values for the standard deviations of the eleven silica results of G-1 and ten of W-1 are to be expected as the selection of the analysts for the glass depended upon the degree to which their results for G-1 and W-1 approached the arithmetic means of the original results. What would not have been expected is that the dispersion of the silica results for the glass should show no improvement upon that of the original thirty-four results for standard rocks.

In considering the data supplied by the eleven laboratories the fact that the standard deviation of the results for the glass is somewhat higher than the corresponding figures for G-1 and W-1 is not of itself important, provided that the average or arithmetic mean is of the same overall standard for the three sets of data, i.e. the deviations of the arithmetic means from the true values should be the same. The increased dispersion of the results for the glass shows that we cannot assume this to be so. We can, however, make a more decisive comparison between the results of the eleven laboratories by rejecting the results not in the range ($\bar{x} \pm 2s$) as described in *Method I*. The values then obtained are 72.66% SiO_2 , 14.00% Al_2O_3 in G-1 and 52.74% SiO_2 , 14.92% Al_2O_3 in W-1.

The revised values for the silica and alumina contents of the two standard rocks as determined by the four *Methods* are summarized in Table 1. Of the four sets of values, those obtained by *Method IV* are probably closer to the actual values for G-1 and W-1 than those obtained by *Methods I, II and III*.

The systematic error that gives rise to the need for corrections to the silica and alumina figures should not arise when direct photometric methods are used. The application of such methods to G-1 and W-1 has been described by a number of authors (Table 2) and the results obtained by one of them (RILEY, 1958) agree closely with the revised value calculated as above by *Method IV*.

PHOTOMETRIC METHODS FOR SILICA AND ALUMINA

The use of photometric methods for the determination of silica and alumina is well established, although a number of difficulties arise in applying them to the analysis of silicate rocks.

The available methods for the photometric determination of silica, based either upon the yellow silicomolybdate complex or upon the blue reduced compound, are not capable of great precision unless care is taken to duplicate exactly the conditions under which the colours are formed. Small differences of acid concentration, molybdate concentration, temperature and the presence of interfering elements all affect the colour densities.

In the photometric determination of alumina by reaction with aluminon, alizarin red-S, ferron or 8-hydroxyquinoline, a prior separation of the aluminium from iron as in the gravimetric method is normally required. It is possible to determine alumina photometrically in the presence of one or more interfering elements as for example in the ferron method (SHAPIRO and BRANNOCK, 1952) where corrections can be applied for the presence of iron and titanium, and in the alizarin red-S method (SHAPIRO and BRANNOCK, 1956) where the interference from iron can be eliminated by conversion to ferrous ferricyanide. Such methods as these will not be applicable to all silicate materials especially where these contain only a little alumina or much iron and titanium.

Furthermore, the accuracy of the results obtained will be dependent upon the choice of standards. To use analysed rocks as the basis of instrument calibration may re-introduce errors made during the classical separations.

These limitations must be borne in mind when the results obtained by photometric methods are considered. For example, the figures given by SHAPIRO and BRANNOCK (1956) for G-1 and W-1 are based upon previously analysed material and any error in the latter will be reflected in their results for the standard rocks. KING *et al.* (1955) used sodium silicofluoride as a silica standard which, in view of the somewhat lower results obtained by them, must be suspect. The results given by RILEY (1958), are clearly based upon a more satisfactory material, pure fused silica, but the difficulties involved in determining a major constituent by a method that is dependent upon the precise adjustment of many variables, remain.

In a survey of this problem MERCY (1956), using the photometric method for silica described by SHAPIRO and BRANNOCK (1952), reckons the average error to be 0.6 per cent and the maximum error 1.0 per cent of the amount of SiO_2 present which represents no improvement upon the classical procedures in so far as normal experimental, as distinct from systematic error, is concerned.

OTHER METHODS FOR SILICA AND ALUMINA

Recent developments in the field of silicate rock analysis have included not only photometric procedures but also a number of new gravimetric methods for silica, a titrimetric method for alumina using EDTA (MILNER and WOODHEAD, 1955), and a combined gravimetric and photometric method for silica (JEFFERY and WILSON, 1960). In a recent review VOINOVITCH (1958) has described studies of a number of newer methods for silica including gravimetric determination as the complex salt of silicomolybdate with the organic bases oxine (BRABSON *et al.*, 1948), and quinoline (ARMAND and BERTHOUX, 1953) and as silica following precipitation with hydrochloric acid and gelatine (LONGUET and BURGLEN, 1955); volumetric determination following precipitation as silicomolybdate-quinoline complex (WILSON, 1949) and as potassium silicofluoride (SAJO, 1955); colorimetric

determination by a molybdenum blue method (BUNTING, 1944) and a spectrographic method (MORAND and KIEHL, 1955). All these methods are rapid in operation, but from an examination of the figures given by VOINOVITCH, none of them appears to offer any improvement in precision upon the classical method for silica. The method of ARMAND and BERTHOUX (1953), using gravimetric determination as the quinoline salt of the silicomolybdate complex has been applied by BENNET *et al.* (1958) to silicate materials used in the ceramic industry. A number of improvements were incorporated, but the interference from iron would be sufficient to invalidate the results for many silicate rocks.

In the procedure of MILNER and WOODHEAD (1955) for the determination of alumina, iron and titanium are removed from the rock solution by extraction of their cupferrates with chloroform, the aluminium is precipitated as the insoluble benzoate, complexed with EDTA and the excess reagent titrated with iron solution using salicylic acid as indicator. The results obtained by MILNER and WOODHEAD using this method are included in Table 2.

Table 2. Some reported values for the silica and alumina content of G-1 and W-1 (%)

Reference	G-1		W-1	
	SiO ₂	Al ₂ O ₃	SiO ₂	Al ₂ O ₃
FAIRBAIRN <i>et al.</i> (1951)*	72.24	14.34	52.33	15.17
FAIRBAIRN (1953)*	72.36	14.44	52.34	15.07
FAIRBAIRN (1953) (preferred values)	72.86	13.94	52.69	14.72
SHAPIRO and BRANNOCK (1956)*	72.45	14.5	52.7	15.1
KING <i>et al.</i> (1955)	71.5		50.8	
MILNER and WOODHEAD (1955)*		14.35		14.92
RILEY (1958)*	72.64	14.08	52.65	15.03
JEFFERY (new determinations)		14.02		14.99
		14.04		15.02
		14.09		15.05
JEFFERY and WILSON (new method)	72.60		52.63	
	72.66		52.67	
JEFFERY (revised values, table 1, IV)	72.66	14.00	52.74	14.92

* Average of results given.

A combined gravimetric and photometric procedure for the determination of silica has been devised by JEFFERY and WILSON and will be reported in full elsewhere. In this procedure, the major part of the silica present in the rock is removed as in the classical procedure by evaporation of the rock solution with hydrochloric acid. This part is determined by loss in weight following volatilization with hydrofluoric acid in the usual way. The minor part of the silica is then

determined in the filtrate by a photometric molybdenum blue method. Results obtained by this method for G-1 and W-1 are included in Table 2. The objections raised against the use of photometric methods for major amounts of silica are not applicable when, as in this case, the silica content of the solution has been reduced to a few milligrams.

Alumina figures for the two rocks obtained by gravimetric determination as oxinate using the procedure described by HILLEBRAND and LUNDELL (1953, p. 124) are also included in Table 2 (JEFFERY, new determinations). The extraction procedure of MILNER and WOODHEAD (1955) was used to effect a separation from iron and titanium. The precipitated complex of aluminium with the oxine reagent was examined spectrographically and found to contain traces of manganese and calcium and rather more than a trace of magnesium (0.02 per cent of the rock).

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Selenium and tellurium content of stony meteorites by neutron activation

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Abstract—By neutron activation analysis the Se- and Te-content of four chondritic meteorites have been determined. The average content is 9.8 ± 2.5 and 0.61 ± 1.7 p.p.m., respectively. These values are lower than those already reported in the literature.

INTRODUCTION

SEVERAL authors (Suess and Urey, 1956) have published data on the relative abundance of the chemical elements. In theoretically deriving these abundances extensive use has been made of certain systematic properties of nuclei because the necessary experimental data are lacking or unsatisfactory. Reliable experimental values of the abundance of each element are of great interest to cosmologists since the abundances of the elements are the result of cosmic events and any useful theory of the origin of the elements has to account in detail for the abundance curve.

A recent theory requires several different types of synthesizing processes in order to explain the features of the abundance curve (Burbidge *et al.*, 1957; Cameron, 1957). Two of these processes are different types of neutron capture. Neutron capture on a long time-scale is thought to be responsible for the abundance peaks at Y (fifty neutrons), La (eighty-two neutrons) and Pb (126 neutrons) while neutron capture on a very short time-scale produces abundance peaks (Coryell, 1956) at approximately Br, Xe and Pt.

Since the abundance of bromine, krypton, iodine and xenon are inherently difficult to determine, reliable data on the abundances of selenium and tellurium would be valuable in establishing the magnitudes of the peak yields at Br and Xe. Byers (1938) reported a selenium content of 13 and 10 p.p.m. in the chondrites, Allegan, Michigan and Tabor, Russia, respectively. The data on tellurium are very uncertain and Suess and Urey (1956) report an interpolated value. Since the chemical and physical properties of selenium and tellurium are very similar, the abundance ratio is a more meaningful quantity than the individual absolute abundances. The Se/Te abundance ratio should thus be rather constant from one meteorite to another. Goldschmidt (1954) estimated a Se/Te atomic ratio of 80 from the data by the Noddacks, and Suess and Urey chose a value of 14.5 while pointing out the need for additional experimental data.

The present paper reports a new determination of the concentrations of selenium and tellurium in chondrites which are supposed to contain the non-volatile elements in relative cosmic abundances. The method of neutron activation was

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applied which for the analysis of trace elements has many advantages over conventional analytical techniques, one of the important advantages being the elimination of reagent contamination.

EXPERIMENTAL

Irradiation

Powdered meteorite samples of from 50 to 200 mg were packaged in aluminium foil and irradiated with various neutron monitors in the Argonne CP-5 heavy-water reactor. The selenium and tellurium content of the aluminium foil was low enough so that contamination from the wrapping material was negligible.

Two types of flux monitors were employed. One group was prepared by introducing a known amount of natural selenium or tellurium (an amount at least fifty times the original content) into a meteorite matrix. These monitors were chemically processed in a manner similar to the samples of unknown selenium and tellurium content. The other group of flux monitors was prepared by evaporating a known amount (5–10 μg) of selenium or tellurium in solution onto filter papers which were wrapped in aluminium foil before irradiation. Both monitors gave identical results for selenium and tellurium, indicating that neutron attenuation in the meteoritic material does not affect the results of the activation analysis.

The selenium content in the meteorites was determined by neutron capture of Se^{74} (0.87 atom per cent in normal selenium; neutron capture cross-section of 26 barns). The neutron capture product is $^{128}\text{d}\text{Se}^{75}$ which is easily detected and identified by three intense γ -rays of 136, 267 and 402 keV. With suitable irradiation and decay periods, the γ -rays associated with selenium activities produced by neutron capture on the other stable isotopes of selenium do not interfere with a quantitative measurement of the intensity of the γ -rays of Se^{75} . Even though a shorter irradiation time and a greater sensitivity (SCHINDEWOLF, 1958) of selenium can be achieved by measuring the radiations of other selenium isotopes produced by neutron activation, Se^{75} is the most convenient isotope for the neutron activation analysis of the element. The meteorites were irradiated for about 1 week prior to the selenium analysis.

The tellurium content of the meteorites was determined from the β -activity of the 9.4 hr Te^{127} formed with a 0.8 barn cross-section by neutron capture on Te^{126} (18.7 atom per cent in normal tellurium). Shorter-lived tellurium isotopes produced by neutron capture were not considered because they necessitated very rapid chemical separation, and the longer-lived isotopes were excluded since they are less sensitive than Te^{127} for tellurium analysis by neutron activation. The meteorite samples were irradiated for about 12 hr for the tellurium analyses.

Chemical separation

The chemistry of selenium and tellurium is very similar and the same procedures were used initially in both analyses to separate these elements from the remainder of the sample. After neutron irradiation and a suitable decay time, about 20 mg of either selenium or tellurium and 1 to 2 g of sodium peroxide were added to the powdered meteorite and fused in a nickel crucible. After a cooling period,

the solid cake was dissolved in 6 N HCl. Selenium and tellurium were then precipitated as the element from a boiling solution by reduction with SO_2 gas. Further purification was achieved by a modification of the procedure by GLENDENIN (CORYELL and SUGERMAN, 1951). Selenium and tellurium were dissolved in aqua-regia, the solution was made basic with NH_4OH , and ferric iron added as a scavenging agent for impurities which coprecipitate with $\text{Fe}(\text{OH})_3$.

A separation of selenium from tellurium was achieved on a Dowex-1 (100–200 mesh) anion exchange column which was 0.8 cm in diameter and 4 cm in length (SCHINDEWOLF, 1957). Selenium was eluted from the column with from three to five column volumes of 3 N HCl, while tellurium is strongly adsorbed (distribution coefficient of 10^3). Such a procedure can give a separation factor of selenium from tellurium of greater than 10^4 . Tellurium is then eluted rapidly with 0.2–0.5 N HCl. The selenium and tellurium samples were prepared for counting by another precipitation with SO_2 , filtration and mounting. Chemical yields in all experiments ranged between 50 and 80 per cent. The efficiency of the chemical separation procedure was tested with radioactive tracers of a number of typical elements such as Ag, Ce, Co, Cs, Hg, Ir, Nb, Ru, Sb, Sc, Ta, Zn and Zr. Decontamination factors of greater than 10^4 were found for all these elements.

Counting techniques

The selenium γ -rays were detected and analysed with a 3 in. by 3 in. NaI(Tl) scintillation crystal coupled to a 256-channel spectrometer. The quantitative analysis for selenium in each of the various meteorites was made by comparing the Se^{75} γ -ray activity of each of the irradiated meteorites with the correspondingly irradiated selenium monitor. Their spectra were indistinguishable except for intensity and no γ -rays due to contaminating activities were detected. Decay measurements of the γ -rays from the meteorite selenium and the flux monitor selenium gave the same half-life. With our experimental conditions approximately 2×10^4 γ -ray counts/min of Se^{75} were observed per μg of selenium.

The 9.4-hr Te^{127} β -activity was counted with an end-window proportional counter. Tellurium (1 μg) gave approximately 10^5 Te^{127} β -counts/min. The decay of the tellurium samples from the meteorites and of the tellurium flux monitors was followed for 24 hr. The decay curves of the meteorite tellurium and the flux monitor tellurium were parallel in all cases except for one Holbrook sample. γ -Ray analysis of this sample revealed the presence of 77-hr Te^{132} with its 2.3-hr I^{132} daughter. The latter tellurium isotope resulted from the fission of uranium with which this Holbrook sample was contaminated. An estimate of the amount of 9.4-hr Te^{127} for this meteorite was made by an analysis of the β -decay curves. The Te^{127} is assumed to result only from the neutron activation of Te^{126} . This is a reasonable assumption because the fission yield of the 127-mass chain is much less than the 132-mass chain and besides this yield is held up at the 93-hr Sb^{127} .

An attempt was made to separate the tellurium from the meteorite before irradiation by first dissolving the meteorite in a HClO_4 –HF solution and then coprecipitating the tellurium with highly-purified selenium. This experiment failed due to substantial loss of tellurium even though the coprecipitation is known

to be almost complete. The tellurium was probably lost as volatile TeF_4 and/or TeF_6 during the dissolution with HF .

RESULTS AND DISCUSSION

The results of the Se and Te activation analysis for several of the stony meteorites are listed in Table 1.

Table 1. Selenium and tellurium content of meteorites

Meteorite	Selenium (p.p.m. by weight)	Tellurium (p.p.m. by weight)	Se/Te (weight ratio)
Chondrites			
Beardsley	10.8	0.88	12.3
Forest City	8.6	0.46	18.7
Holbrook	13.3	0.62	21.4
Modoc	6.5	0.46	14.1
Achondrites			
Johnstown, Colo.	0.007	0.007	
Nuevo Laredo	0.0016		
Brenham, Kansas	5.8		

Each entry in Table 1 is an average of two independent determinations and is believed to be accurate to within about 15 per cent except the tellurium content of Holbrook where an error of 50 per cent is likely. The values of selenium and tellurium in Johnstown, Colo., are upper limits. The average selenium and tellurium contents of the chondritic meteorites Beardsley, Forest City, Holbrook and Modoc are 9.8 ± 2.5 p.p.m. and 0.61 ± 0.17 p.p.m., respectively. The atomic abundances of these elements relative to silicon $= 10^6$ have been calculated and are listed in Table 2 along with values derived by other authors. The relative weight of silicon in primitive solar non-volatile material is taken as 18.5 per cent.

Table 2. Cosmic atomic abundances of selenium and tellurium

	GOLDSCHMIDT	UREY	SUESS and UREY	This paper
Se	13.5	24	67.6	18.8
Te				0.73
Se/Te	80	150	14.5	25.8

The data on the Se- and Te-content of chondritic meteorites presented here are lower than previously assumed and indicate that the abundance peaks around the elements Br and Xe which are caused by neutron-capture processes on a short time scale, are lower than reported. It would be too hasty, however, to reconstruct the abundance curve without a better knowledge of the abundance of neighbouring elements such as As, Rb and Sr, and Sb, Cs and Ba. The abundance of the elements Br and Kr as well as I and Xe can be obtained by interpolation only because, owing to their volatility, no reliable data for these elements will be available from analysis of meteorites. It therefore seems necessary to wait for new analytical data of the As, Rb, Sr, Sb, Cs and Ba content of meteorites.

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GEOCHEMICAL NOTES

Silver and thallium contents of rocks

PRIOR to the recent study of HAMAGUCHI and KURODA (1959) little information has been available on the distribution of silver in igneous rocks. In order to attain the necessary analytical sensitivity, these investigators used a procedure involving chemical enrichment followed by spectrochemical analysis (HAMAGUCHI and KURODA, 1957). We have recently determined silver in some rocks by neutron-activation analysis and feel that our results may be of interest. In our analytical method both silver and thallium were determined in 1 g samples. Full details of the procedure will be published elsewhere.

In Table 1 are shown our results for the standard granite G-1 from Westerley, Rhode Island, and for the standard diabase W-1 from Centreville, Virginia. The data for thallium

Table 1. Silver and thallium analyses of the standard granite G-1 and standard diabase W-1

G-1		W-1	
Silver content (p.p.m.)	Thallium content (p.p.m.)	Silver content (p.p.m.)	Thallium content (p.p.m.)
0.047	1.3	0.055	0.15
0.046	1.1	0.055	0.17
0.048	1.2	0.058	0.17
0.036	1.4	0.058	0.18
0.038	1.0	0.057	0.17
0.037	1.5	0.058	0.16
0.044	1.0	av. 0.057	av. 0.17
0.042	1.5		
0.043	1.4		
av. 0.042	av. 1.3		

appear to be independently confirmed by results obtained by the ion-exchange and spectrographic technique of EDGE *et al.* (1959), namely 1.3 p.p.m. Tl in G-1 and 0.1 p.p.m. Tl in W-1 (AHRENS, private communication).

Table 2 records the results obtained by us for the silver and thallium contents of a series of rocks supplied by Dr. J. R. BUTLER, Department of Geochemistry, Imperial College, London. The arrangement corresponds to the geological differentiation succession of the rocks in the Insh Mass, (mostly gabbro), Aberdeenshire.

In general the silver contents reported here seem to be similar to those found by HAMAGUCHI and KURODA (1959) in corresponding Japanese rocks. This helps to provide some

Table 2. Silver and thallium in rocks of the Inch Mass, Aberdeenshire

Sample no. (Dept. of Geology, Imperial College, London)	Rock	Location	Silver found (p.p.m.)	Thallium found (p.p.m.)
3722(H63)	Peridotite	W slope of Hill of Barra	0.030	1.03
			0.028	1.06
			0.030	1.04
			0.028	1.04
3724(H67)	Pyroxenitic peridotite	As above	0.086	
			0.078	
3732(H55)	Olivine gabbro	NE top of Gallow Hill, Leslie	0.037	0.047
			0.041	0.049
			0.038	0.046
			0.042	0.048
3645(H107)	Syenogabbro	S slope of Gallow Hill	0.44	0.046
			0.46	0.045
			0.47	0.047
			0.43	0.045
3731(H51)	Syenite	SW slope of Gallow Hill	0.040	0.31
			0.032	0.28
			0.039	0.26
			0.038	0.26
			0.040	0.34
			0.036	0.26
			0.033	0.31

further justification for their calculation of the crustal abundance of silver as 0.08 p.p.m. In addition, our analytical results for thallium can be correlated quite well with the data obtained by other workers for similar rock types (SHAW, 1957).

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The possibility of *d*-electron coupling in olivine at high pressures

CLARKE (1959) has discussed various types of transitions, including electronic transitions, which may occur in materials subjected to very high pressures and RINGWOOD (1958) has presented convincing evidence that $(\text{Mg,Fe})_2\text{SiO}_4$ may change from an olivine to a spinel structure within the mantle of the earth. There is in addition, a type of electronic transition not mentioned by CLARKE which could occur with Fe_2SiO_4 and which appears a most probable process with pressures available in the mantle. It is the purpose of this note to suggest that contraction may occur due to coupling of *d*-electrons in the ferrous ion.

It is well known that in a field-free transition-metal ion such as Fe^{2+} the *d*-electrons are fully degenerate (i.e. the energy of the five *d*-orbitals are identical). The electronic arrangement of the six *d*-electrons of the ferrous ion would be as indicated in (a) Fig. 1. When the ion is placed in a negative octahedral field such as that produced by six oxygens surrounding the ion, the degeneracy of the *d*-levels is destroyed and the orbitals become grouped into two sets of unequal energy. In the terminology of ligand-field theory (GRIFFITH and ORGEL, 1957) these sets comprise three orbitals of low energy (t_{2g}) and two orbitals of higher energy (e_g). These are related to the different spatial configurations of the *d*-orbitals in relation to the octahedral field (see GILLESPIE and NYHOLM, 1957). In many cases this splitting of the *d*-levels gives rise to the absorption observed in the visible regions of the spectrum. The difference in energy of the levels may thus be estimated from the position of these absorption bands (ORGEL, 1955).

If the splitting of the levels becomes sufficiently large, the electrons may obtain from coupling sufficient energy to overcome a repulsion barrier (also deduced from spectra) and may pair-off, giving a new electronic configuration in which Hund's rule does not apply. Thus for the ferrous ion we may have the three configurations illustrated in Fig. 1.

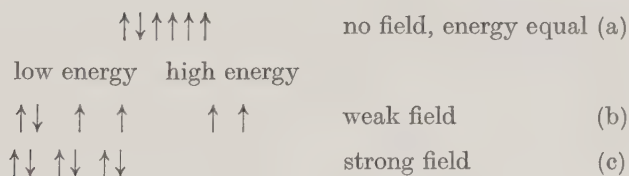


Fig. 1. Possible electron configurations in Fe^{2+}

Normally, when coupling such as (c) occurs, there are changes in the magnetic properties (in the case of Fe^{2+} a change from paramagnetism to diamagnetism) and at the same time there is a considerable change in the size of the ion. It is difficult to obtain examples of such changes in simple binary compounds for in most of these the field is too weak to cause coupling; the most familiar examples involve complex ions. With these there may be added complexities (e.g. in $\text{Fe}(\text{CN})_6^{-4}$) such as multiple bonding in the coupled species due to better hybrid bonds. In general, a coupled ion will form stronger covalent bonds for the same reason. In the hydrated ferrous ion $\text{Fe}(\text{H}_2\text{O})_6^{2+}$, which is paramagnetic, the d^2sp^3 -octahedral hybrid which is formed from 4*d*-, 4*s*-, 4*p*-orbitals of the iron, will allow weaker covalent bonding than in a coupled, diamagnetic species where 3*d*-, 4*s*-, 4*p*-orbitals would form the hybrid. Conversely, as bonds become more covalent there is an increased possibility of coupling.

In the present discussion the most important aspect of the coupling process is related to the volume decrease associated with it and we may consider two examples to illustrate this effect. The first row transition metal ions are similar in size and show a gradual contraction with increasing atomic number. The ionic radii of Fe^{2+} and Mn^{2+} given by

PAULING (1948) are 0.75 and 0.80 Å respectively. We would thus expect that Fe—X linkages would be only a little shorter than Mn—X linkages and this is certainly true in the majority of cases. But in the iso-structural disulphides, pyrite and hauerite, a serious departure occurs. With MnS_2 the Mn—S distance of 2.59 Å is close to the radius sum of 2.64 Å while with FeS_2 the Fe—S distance of 2.27 Å is much smaller than the radius sum of 2.59 Å. This contraction may be correlated with normal paramagnetism for MnS_2 and coupling giving diamagnetism in FeS_2 (NÉEL and BENIOT, 1953). In neither case should the degree of covalency be very different on the basis of simple electronegativity considerations. It is interesting to note that in the iodides MnI_2 and FeI_2 which should be equally covalent, the distances are similar and no coupling occurs. That FeS_2 could be coupled while MnS_2 is not, might be expected, for the coupling energy of the *d*-electrons in Mn^{2+} is much greater than in Fe^{2+} , a reflection of the general stability of half filled *d*- and *f*-shells (the coupling energy of Mn^{2+} is 146 kcal compared with 100 kcal for Fe^{2+}).

A second example of this contraction may be taken from the complexes of cobalt. The normal ionic radii of Co^{2+} and Co^{3+} are 0.72 and 0.63 Å, respectively. The Co—N distance in the spin-free complex $\text{Co}(\text{NH}_3)_6^{2+}$ is 2.5 Å and by analogy a distance of 2.4 Å would be predicted in $\text{Co}(\text{NH}_3)_6^{3+}$. The measured distance in the latter diamagnetic complex is actually 1.9 Å illustrating the extreme value of the contraction in a case where there can be little multiple bonding (PARRY, 1950). ORGEL (1956) has also mentioned the expected contraction on coupling.

If it is considered reasonable that contraction occurs with electron coupling, it follows that coupling will be induced by pressure. It remains to examine the energies involved and the volume changes, to see if coupling is feasible in the mantle of the earth. Such transitions cannot occur in the metallic phase of the core as almost all the *d*-electrons are already involved in bonding in the metal.

Considering the specific case of olivine, to calculate the pressure of transition between paramagnetic and diamagnetic forms the following information is needed: the coupling energy of *d*-electrons in Fe^{2+} , the splitting of the *d*-levels in olivine, the effect of pressure and temperature on the splitting, the volume change associated with the transition. The coupling energy should be fairly independent of the environment, and GRIFFITH and ORGEL (1957) give a value of 50 kcal per electron. The splitting energy can be obtained from the absorption spectrum of olivine, and we may use a value of 27 kcal per electron from the data of CLARKE (1957). The selection of the band at 9600 cm^{-1} is based on analogy with the value for the hydrated ferrous ion. McCURE (1957) found that band shifts in oxygen co-ordinated cations are generally rather slight, a feature which will be discussed elsewhere. Thus at standard pressure and temperature the energy barrier is near 46 kcal/mole of ferrous ion. No data are available to allow estimates of the effect of pressure and temperature on the splitting in olivine. PARSONS and DRICKAMER (1958) have studied the effect of pressure on the spectrum of ions such as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$ and found a marked increase in splitting with pressure as would be expected from bond shortening with compression. Temperature will operate in the opposite direction, but if at depth the net effect is to decrease the molar volume, then one might anticipate increased splitting.

There are insufficient data on radius changes with coupling to allow any precise estimate of the expected volume change in fayalite. From the two examples listed above, a change of 0.1 Å does not appear excessive. With such a value the molar volume of diamagnetic fayalite would be similar to forsterite and the ΔV of transition would be about $3\text{ cm}^3\text{ mole}^{-1}$. A transition would be expected at depths of the order of 1400 km. This estimate indicates pressures in excess of those found by RINGWOOD for the spinel transition so that coupling may be more likely to occur in the spinel modification. With the contraction used above, which may well be an underestimate, if the olivine in the mantle contains 10 mole

per cent fayalite, then the phase and electron changes in fayalite will account for 18 per cent of the volume reduction in olivine.

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A search for variations in the natural abundance of uranium-235

MANY papers have been published during the last 10 years which discuss observed variations in the natural abundances of certain light elements such as oxygen, nitrogen, sulphur and boron, but references to uranium are very scanty. Because the weights of the principal isotopes of uranium differ by only approximately 1 per cent, any variations in relative abundance resulting from naturally-occurring separation processes are likely to be small, and therefore only detectable by refined techniques. This Note describes the results of a comparison of the isotopic compositions of the uranium in twelve ore concentrates by high-precision gas-source mass spectrometry.

The maximum possible percentage deviation (Di) of the isotope ratio of a given ore from that of the mean is given by adding together the measured percentage deviation and the error assigned to it, without regard to sign. That is to say,

$$Di = \left| \frac{R_i - \bar{R}}{\bar{R}} \right| \times 100 + \left| \frac{\delta R_i}{\bar{R}} \right| \times 100$$

where R_i are the individual measured ratios, δR_i the errors of measurement assigned to them, and $\bar{R}$ is their arithmetic mean. The equation is true within whatever confidence limits are ascribed to δR_i . In the present Note, R refers to the ratio U^{238}/U^{235} , and all results are quoted with errors corresponding with the 95 per cent confidence limits unless otherwise stated.

Measurements on uranium were pioneered by NIER (1939), who examined three ores and quoted figures from which it can be shown that $D_{\max}$, the largest of the three values of D for the set of ores, is given by

$$D_{\max} = \left| \frac{138.9 - 138.9}{138.9} \right| \times 100 + \left| \frac{1.3}{138.9} \right| \times 100 = 0.93 \text{ per cent}$$

Recently SENTLE *et al.* (1957) described an examination of thirteen ores, including eleven from the Colorado Plateau, and their results (excluding one ore whose measurement was in doubt experimentally) give

$$D_{\max} = \left| \frac{137.7 - 137.7}{137.7} \right| \times 100 + \left| \frac{0.64}{137.7} \right| \times 100 = 0.46 \text{ per cent}$$

LOUNSBURY (1956) quotes an earlier paper by FOX and RUSTAD (1946), stating that other workers in their laboratory had compared two ores from South Africa with other ores from Canada and the Colorado Plateau and showed that differences were less than 0.03 per cent, but as no other information was provided it is difficult to interpret this statement. Also, SENTLE *et al.* point out that discrepancies in lead dating measurements might be explained by small variations in the uranium isotopic composition, and that this fully warrants further investigation.

In the present work, the uranium was completely extracted from each of twelve ore concentrates obtained from various parts of the world; impurities were removed chromatographically and the purified uranium, as U_3O_8 , was converted to uranium hexafluoride. Samples of each ore were then compared with a bulk natural standard on a Metropolitan-Vickers M.S.2 spectrometer fitted with a molecular-beam source as described by MCKNIGHT (1959), using the method of double collection. In this way the U^{235} abundances of two samples could be compared with a relative accuracy of 0.06 per cent, this figure being the standard deviation for a single comparison lasting 20 min. The errors quoted in Table 1 are 95 per cent confidence limits of the mean of a number of comparisons. Details of the origins of the various ores are shown in the Table 1, together with the results of the comparison measurements.

Table 1

Designation of ore or deposit	Location	$\frac{R - \bar{R}}{\bar{R}} \times 10^3$	D (%)
Wheal Edward	Cornwall, England	-0.01 ± 0.24	0.025
Magnesia Uranium Concentrate	Portugal	$+0.03 \pm 0.38$	0.041
Shinkolobwe, pitchblende	Belgian Congo	-0.06 ± 0.40	0.046
Shinkolobwe, "Ionex"	Belgian Congo	$+0.24 \pm 0.22$	0.046
Mindola, Lot 1	Northern Rhodesia	-0.07 ± 0.21	0.028
Mindola, Lot 4 (high-copper content)	Northern Rhodesia	$+0.06 \pm 0.18$	0.024
South African Concentrate	The Rand, South Africa	-0.03 ± 0.30	0.033
Rum Jungle	Northern Australia	-0.12 ± 0.26	0.038
Mary Kathleen	Queensland, Australia	0.00 ± 0.43	0.043
Radium Hill	South Australia	$+0.01 \pm 0.32$	0.033
Blind River	Ontario, Canada	-0.02 ± 0.26	0.028
Beaver Lodge	Alberta, Canada	-0.08 ± 0.20	0.028

From these figures $D_{\max} = 0.046$ per cent. It follows that, within the limits of 95 per cent confidence, variations in the relative abundance of the principal isotopes of uranium are less than 0.05 per cent. With the current developments in high-precision mass spectrometry at R. and D. Branch, Capenhurst, it will be feasible to obtain higher precisions in these comparisons of natural ores.

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Mordenite synthesis in a natural hydrothermal solution

At Wairakei, New Zealand, numerous bores have been drilled into a hydrothermal system to provide steam for a geothermal power station. The hydrothermal system and bore field have been described previously (GRANGE 1955; STUDD 1958), and a description has been given of the hydrothermal alteration at various levels in the country (STEINER, 1953).

It is always uncertain whether temperatures measured at various depths in the completed drill-holes can be equated exactly with the temperatures which previously existed in the undisturbed field. Uncertainties also exist as to the exact original chemical environment at a given level.

The opportunity was taken recently of exposing a natural obsidian glass to the hot solution deep within a bore. The resultant crystallisation was, it is believed, the first controlled hydrothermal mineral synthesis using an analysed natural solution. Natural glass is a convenient reactive starting material. Its major element analysis was as follows (Analyst, J. A. Ritchie, Dominion Laboratory):

SiO₂, 67.98%; Al₂O₃, 12.10%; Na₂O, 3.08%; CaO, 2.74%;
 K₂O, 1.29%; Fe₂O₃, 1.18%; FeO, 0.94%; MgO, 0.22%;
 TiO₂, 0.22%; H₂O+, 6.89%; H₂O—, 3.17%.

The powdered glass was placed in a platinum tube left slightly open at one end to allow water to enter. This was suspended at a depth of 1045 feet in Bore 31 in the centre of the field. The temperature measured at this point was 230°. During the experiment the bore was allowed to bleed slowly to maintain the temperature, and continuously provide fresh solution around the material.

The glass was amorphous to X-rays before immersion, but after 17 days exposure it gave a strong X-ray powder pattern in complete agreement with that published for the zeolite mordenite (HARRIS and BRINDLEY, 1954). The diffraction pattern did not reveal any other crystalline mineral.

The composition of the reactive water phase at 230° was calculated from separate analyses of the water and steam phases which are formed by adiabatic expansion, and are discharged from the bore at the surface. From an estimate (ELLIS and FYFE, 1957) of the

first apparent dissociation constant of carbonic acid in water at 230° the approximate pH of the solution was also calculated. The environment in which mordenite formed is distinctly acid with respect to neutral water (pH 5.7) at a temperature of 230°.

Water composition at 230° (p.p.m.)

$\text{Li}^+ = 9.6$	$\text{CO}_2 = 300$	$\text{Cl}^- = 1550$
	$\text{SiO}_2 = 390$	
$\text{Na}^+ = 905$	$\text{H}_2\text{S} = 15$	$\text{SO}_4'' = 41$
$\text{K}^+ = 144$	$\text{As}_2\text{O}_3 = 4.5$	$\text{HCO}_3' = 14$
$\text{Rb}^+ = 1.6$	$\text{H}_3\text{BO}_3 = 117$	$\text{F}' = 4.7$
$\text{Cs}^+ = 1.8$	$\text{pH} = 4.7$	$\text{HS}' = 2$
$\text{Ca}^{++} = 15$		
$\text{Mg}^{++} = 4$		
$\text{NH}_4^+ = 1.2$		

It is now appropriate to correct two common misconceptions concerning this type of work. First, the term "alkaline thermal area" which is often applied to chloride water hydrothermal systems such as Wairakei, gives a wrong impression of their chemical nature. Secondly, the experiment above is sufficient proof that zeolites do not crystallize only from alkaline solutions.

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LETTER TO THE EDITOR

An attempt to synthesize graphite by the dissociation of carbon dioxide—the experiment of K. FRAUENFELDER

SEVERAL years ago interest was aroused concerning the validity of using C^{12}/C^{13} ratios as a means of distinguishing biogenic–nonbiogenic carbon in rocks older than 10^9 years (RANKAMA, 1948, 1954; CRAIG, 1954). At the time reference was made to the experimental results of FRAUENFELDER (1924) in which he observed the formation of graphite crystals within the walls of a silica glass tube through which CO_2 was passing at $1100^\circ C$ and 2–3 atm. pressure. By a series of experiments he concluded that silica had a catalytic effect on the dissociation of CO_2 to graphite and oxygen.

CRAIG (1954) maintained that these results were impossible since the equilibrium constant for this dissociation is only of the order of 10^{-21} at $1000^\circ K$. However, FRAUENFELDER's experiments were not performed under equilibrium conditions; fresh gas entered the system periodically. Furthermore, CRAMER and WEYL (1950) observed the non-equilibrium reduction of N_2 to produce ammonia at elevated temperatures in a system containing H_2O and ground silica gel. They attributed their results to catalysis on hydrated silica surfaces. Hence, it was believed worthwhile to attempt to reproduce FRAUENFELDER's results on the possibility that silica would act as a rate-promoting catalyst under non-equilibrium conditions.

FRAUENFELDER's apparatus and conditions were reproduced with the exception that all rubber fittings were replaced by polyethylene because of its low volatile content. Numerous runs were made at various rates of gas flow (0 cc/min.–50 cc/min.), lengths of time (1–18 hrs.), pressures (1–3 atm.), and temperatures (500° – $1150^\circ C$). Under no set of conditions was graphite observed to form. Additional runs were made using all rubber fittings (higher volatile content) and in one case minute, unidentifiable black specks were observed on the tube walls.

It must be concluded that even under the non-equilibrium conditions of these experiments the results of FRAUENFELDER have no validity. It is puzzling, nevertheless, that he did observe, and photograph, well-formed hexagonal graphite crystals. The partial oxidation of organic volatiles produced from heated rubber fittings cannot account for the quantities of graphite that were formed. In fact, one of his experiments was carried out with excess O_2 , burning graphite at one end of the tube and obtaining crystals in the tube walls at the other end. RANKAMA (written communication) suggests that FRAUENFELDER may have used old and contaminated tubing that had been lying around a laboratory for years. This might account for the fact that the bulk of the crystals were found contained within the tube walls.

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ERRATA

E-AN ZEN: Carbonate equilibria in the open ocean Geochim. et Cosmochim. Acta **18**, 57-71.

On p. 64 "43 per cent" should read 4.3 per cent.

"46 per cent" should read 4.6 per cent.

Papers to be published in future issues

- J. F. LOVERING, L. G. PARRY and J. C. JAEGER: Temperature and mass losses in iron meteorites during ablation in the earth's atmosphere.
- G. G. GOLES, R. A. FISH and E. ANDERS: The record in the meteorites—I. The former environment of stone meteorites as deduced from K^{40} -AR ^{40} ages.
- W. H. R. SHAW: Studies in biogeochemistry—I. A biogeochemical periodic table. Studies in biogeochemistry—II. A biogeochemical periodic table. Discussion and references.
- G. JURAIN: Moyens et résultats d'étude de la radioactivité due au radon dans les eaux naturelles.
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